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Adsorption of Copper on Iridium

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ABSTRACT

The work described in this paper is a study of copper adsorption on the whole tip surface of iridium field emitter. The study has been carried out using Field Emission Microscope. Changes in electron work function (Φ) of the iridium substrate, which are produced by vapour deposition of submonolayer of copper in Ultra High Vacuum (UHV), have been measured by noting the changes in the slope of Fowler-Nordheim (FN) plots.

1. Introduction

Electron emission from a low temperature metal into a vacuum under the influence of a high electric field at the surface is called field emission and was first observed by Wood in 1897 (Wood 1897). Field emission microscopy (FEM) is an analytical technique used in material science to investigate molecular surface structure and their electronic properties (Egemen 2011). Invented by Erwin Müller in 1936, the FEM was one of the first surface analysis instruments that approached near- atomic resolution.

In contrast to other types of electron emission in which energy must be supplied to enable electrons to surmount the surface potential barrier, field emitted electrons are transmitted through the potential barrier from energy states near Fermi level (Cutler et al., 1965).

Field emission is independent of temperature up to 1500 K (Gossling 1926). A description based on quantum mechanical tunneling through the potential barrier at the metal surface was given by Fowler and Nordheim (Fowler et al., 1928; Nordheim 1928) in 1928 who successfully derived a relationship between current density (J), applied voltage (V), and electron work function(Φ), which is defined as the minimum amount of energy required to remove an electron from the surface of a metal at 0 K (Gyftopoulos et al., 1962).

Adsorption can be divided into two categories (Gomer 1961), physical adsorption (physisorption) and chemical adsorption (chemisorption). In the first type, the forces involved in adsorbate-substrate bonding are weak. In chemisorption a stronger bond between adsorbate and substrate is formed, the adatoms share electrons with the substrate. The resulting layer often has an electric dipole, which has a marked effect on the electron work function and hence on field emitted current. Metallic adsorption falls in the second category.

In the present study the adsorption of copper on iridium, which has the face-centred cubic (fcc) structure, has been investigated using vacuum techniques and electron work function versus adsorbate coverage plots in an attempt to characterize in some detail the behaviour of this system. Iridium is in Group 9 (VIIIB) of the periodic table with atomic number of 77. Iridium is a transition metal that is also part of the platinum family with electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4f^{14}\ 5s^2\ 5p^6\ 5d^7\ 6s^2$ (Shabalin 2014). The metals in platinum family are also known as the noble metals. They have this name because they do not interact well with other elements and components. Iridium is the chemical element with atomic number 77, and is represented by the symbol Ir. A very hard, brittle, silvery-white transition metal of the platinum family, Iridium is the second-densest element (after Osmium) and is the most corrosion-resistant metal, even at temperatures as high as 2000°C. Iridium metal is employed when high corrosion resistance at high temperatures is needed, as in high-end spark plugs, crucibles for recrystallization of semiconductors at high temperatures, and electrodes for the production of chlorine in the chloralkali process. It is not attacked by almost any acid, aqua regia, molten metals or silicates at high temperatures(DGR Industrial Products, 2012).

Thin films of noble metals, such as iridium, have several potential applications in Integrated Circuits. Noble metals are excellent metals for electrode fabrication because of their chemical stability, highly electrical resistance and many of them withstand highly oxidizing conditions (Shirvaliloo 2015).

Iridium in special is chemically very stable and withstand highly oxidizing conditions (Aaltonen et al.,2004)which are the reasons behind using it to Integrated Circuits and electrodes in dynamic random access memories (DARMs) and ferroelectric random access memories (FRAMs). Other applications in Integrated Circuits include gate electrodes in metal oxide semiconductor field effect transistors (MOSFETs).

2. Experimental

The thermally cleaned tip was held at 78K by cooling it with liquid nitrogen. In the absence of the applied electric field small doses of copper were successively deposited on the iridium emitter and spread evenly over the surface of the emitter by heating the supporting loop at a predetermined temperature for 60 seconds, the time which experiment showed was sufficient for a quasi-equilibrium state to be reached. By measuring the voltage (V) required to draw a certain field emission current before deposition and after equilibrium, the voltage versus coverage (θ) curve was plotted at every spreading temperature (Ts). FN readings were taken when the tip surface was clean (θ = 0) and at every third or fourth equilibrated dose afterwards. The resulting electron work function (Φ) was measured at those points. This procedure was repeated until there was no further change in (Φ) with copper adsorption. At this stage the tip was flash cleaned to remove the adsorbate copper and the whole process was repeated for a different spreading temperature.

3. Results and discussion

Variation of Electron Work Function (Φ) with Copper Coverage (θ) can be depicted. Fig. 1 depicts the voltage (V) versus coverage (θ) at Ts = 380K. The circled points on the curve are the points at which FN readings were taken.

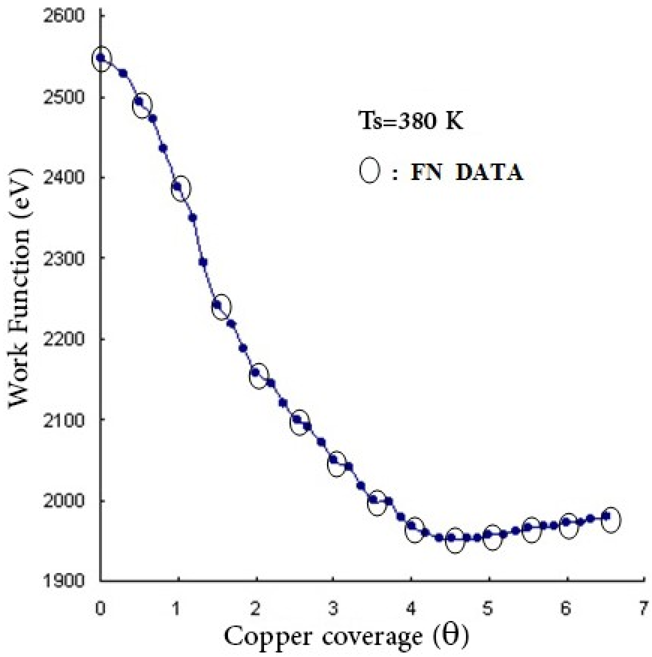

Fig. 1. Change in (V) with Copper Coverage (θ) at Ts = 380 K

For clean iridium tip used as a field emitter in the present work, the electron work function value has been taken to be 5.27 eV (Michaelson 1977: Wilson 1966). Iridium can have work function of about 4.7 eV to about 5.7 eV (Shabalin 2014), for various hkl- indices the electron work function of oriented single crystal is 5.50 eV for (100), 4.85 eV for (110), and 5.74 eV for (111). DP Bernatskii and VG Pavlov in their study of graphene on iridium emitter adopted the value of the average electron work function of iridium to be 5.4 eV (Bernatskii et al., 2011). The electron work function of $Ir_{(111)}$ was taken by Titta Aaltonen to be 5.76 eV (Aaltonen 2005). This value was also adopted by Fabina and his colleagues (Schulz et al., 2014). The average electron work function of iridium was taken by Rosangliana and R.K. Thapa to be 4.928 eV (Rosangliana et al., 2016). The resulting electron work function at the circled points in Fig.1 was measured using the following equation:

$$\Phi_{ad} = \Phi_{cl}\left(\frac{S_{ad}}{S_{cl}}\right)^{2/3} \quad (1)$$

Where Φ_{ad} is the average work function of the adsorbate-substrate surface, S_{ad} is FN slope for the adsorbate-substrate surface, Φ_{cl} is the average work function of the clean surface and S_{cl} is FN slope for the clean surface. Fig. 2 shows the changes in (Φ) with copper coverage obtained at the circled points of Fig. 1, Fig. 3 and Fig. 4 show similar changes at Ts of 437 K and 655 K respectively.

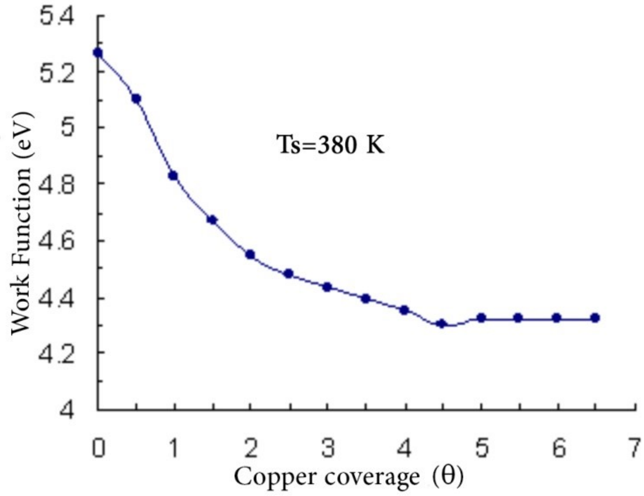

Fig. 2. Change in Electron Work Function with Copper Coverage (θ) at Ts= 380 K

As can be seen from Figs. (2-4) that the increase of copper coverage reduces(Φ) slowly until it reaches to a coverage-independent value (Φ_{sat}). This value has been found to be in the order of 4.18 eV to 4.32 eV depending on Ts. Similar coverage-independent values for (Φ_{sat}) at high coverages had been observed in the adsorption of copper on tungsten (Jones 1965: Cetronio et al, 1974: Melmed 1965).

As can be seen from Figs. (2-4) that the adsorption of copper on a thermally cleaned field emitter iridium tip produces a surface electron work function that is lower than that of the clean iridium surface. The most likely reason for the electron work function decease at low coverage is that the electronegativity of copper is (1.9) which is less than that of iridium (2.2), (Pauling 1960), so that in a copper-iridium dipole the copper atoms are positively charged with respect to iridium as depicted in Fig.5.

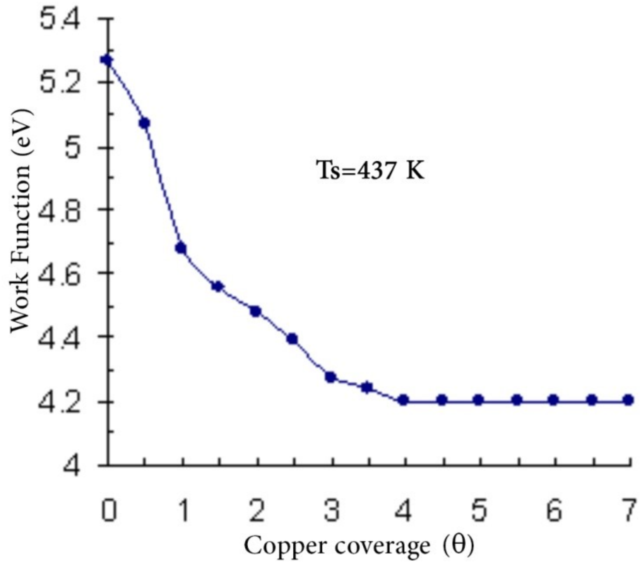

Fig. 3. Change in Electron Work Function with Copper Coverage (θ) at Ts = 437 K

Increasing copper atoms density results in a smooth continuous decrease in (Φ) until it reaches the saturation level (Φ_{sat}) which is found to be dependent on Ts. The decrease in (Φ) at higher coverages may be explained as follows (Anderson et al., 1963). As the copper atoms density increases the density of the copper-iridium dipoles also increases until it reaches a point at which further adatoms will occupy sites relatively far from the iridium surface atoms and the dipoles formed are weak, resulting in little effect on the measured electron work function.

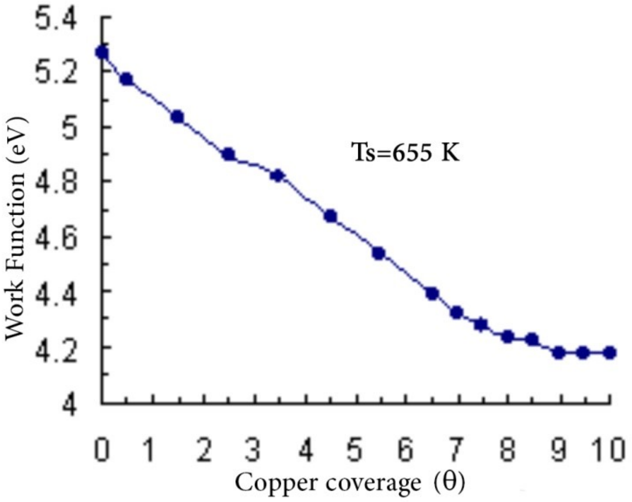

Fig.4. Change in Electron Work Function with Copper Coverage (θ) at Ts = 655 K

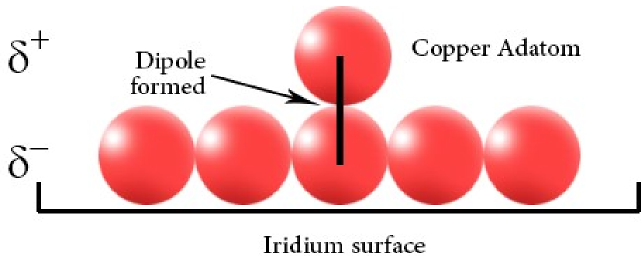

Fig. 5: Electropositive Dipole Formed by Copper Adsorption on Iridium Surface

With increasing copper density still more, the interaction of copper atoms dominates so that copper is establishing its own electronic structure and the electron work function reaches its final constant value (Φ_{sat}) which is believed to represent the work function of bulk copper (Zuber et al., 1979). The final coverage-independent electron work function value obtained in this study lies in the range of 4.18 eV to 4.32 eV, which is considered to be effectively the electron work function of thick adsorbed copper.

4. Conclusions

Adsorption of copper on iridium surface decreases the average electron work function (Φ) at lower coverages. This behaviour is not unexpected. Iridium has an electronegativity of (2.2),while copper has an electronegativity of (1.9) (Pauling 1960), therefore from the electronegativity considerations copper-iridium dipoles should be formed with copper is positively charged with respect to iridium, resulting in a surface with lower electron work function.

With increasing the coverage of copper the electron work function decreases continuously and finally attains the coverage-independent value (Φ_{sat}) which is believed to represent the electron work function of bulk copper. The value of (Φ_{sat}) in this study lies in the range of 4.18 eV to 4.32 eV, which is comparable with that of copper-tungsten, which was found to be 4.30 eV (Jones 1965), and 4.36 eV (Polanski et al., 1973).

It is found that (Φ_{sat}) of copper on iridium is temperature-dependent, but the differences in the final values of (Φ_{sat}) are small at different spreading temperatures.

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