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Measuring the work function of the (100) plane of Iridium electron emitter by probe hole field electron emission microscope.

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Highlights

- **Work function is important in applications involving electron emission from metals, as in photoelectric devices and cathode-ray tubes.**
- **The highest known metal work function is approximately 6.35 eV for platinum (Pt) and lowest work function is 2.14eV for cesium (Cs).**
- **We obtained work function values of 5.80 eV to 6.00 eV for the (100) plane of the iridium metal.**
- **The work function was computed mainly from the current–voltage data using Fowler–Nordheim equation.**

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ABSTRACT

The work described in this paper is a study to measure the work function of the 100 plane (Φ_{100}) of the iridium field emitter surface (the tip). The study has been carried out using a field emission microscope with a probe hole in the centre of the screen, which permitted to examine the individual crystal planes of the tip surface. The work function was computed from the current–voltage data using Fowler–Nordheim equation and a computer program which incorporated a point throwing routine and calculated errors in the measured work function were generally found to be ±0.02 eV or less.

1. Introduction

In previous studies described in (Hashim, 2017; Hashim, 2009; Hashim, 2018) which a simple field emission microscope was used to study the changes of the work function of the iridium field emitter substrate (the tip) with the coverage of silver, copper, and gold, the changes in the average work function (Φ) were derived from the measurement of the total field-emitted current. Most of that current was emitted by the bright regions (on the field emission pattern) of the emitter surface which are known from ion microscopy to be rough on an atomic scale (Ehrlich, 1959; Jones, 1965; Bassett, 1965) and this made it difficult to interpret the observed behavior in detail since the dark regions which ion microscopy has shown to be well ordered on an atomic scale (Ehrlich, 1959; Jones, 1965; Bassett, 1965) contribute very little to the emitted current.

More useful information can be obtained, however, if emission measurements can be made on individual crystal planes. Some authors (Dyke *et al*., 1954; Oguri, 1964) tried to achieve that by measuring the light output of the screen, but it was found to be a difficult and complicated method. Muller (Muller, 1955) introduced a microscope with a probe-hole in the screen, which permitted examination of the different crystal planes of tungsten and obtained experimentally satisfactory results by taking Fowler-Nordheim (FN) plots for several of those planes.

The present work was carried out in an adapted version of the improved Van Oostrom microscope (Van Oostrom, 1966). Fig. 1 illustrates the schematic diagram of this microscope. The anode is made up of a stainless steel disc, which is coated with phosphor, having a 1 mm diameter hole at its centre. The selection of the desired plane can be achieved by centering it over the probe hole by means of a rotatable electromagnet whose pole pieces are located around the constricted neck of the microscope tube where the tip is mounted on the supporting loop. This arrangement was adopted to concentrate the magnetic field in the vicinity of the tip so that regions of the image can easily be deflected over the probe hole and to minimize the magnetic field in the region of the anode.

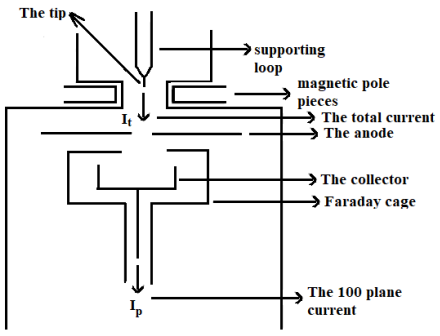

Fig. 1. Schematic diagram of a microscope incorporating a probe hole.

To calculate the work function of a plane (Φ_P), it is necessary to measure the emitted current from that plane, I_P, the total emitted current, I_t, and the voltage V, applied between the anode and the tip. The current density (J) depends on the applied field (F) and work function (Φ) of the electron emitter according to Eq. (1):

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$$J = 1.54x10^{-6}\frac{F^2}{\emptyset\, t_y^2}\exp\left(-6.83x10^7\frac{\emptyset^{\frac{3}{2}}}{F}f(y)\right) \quad (1)$$

Where (J) is in amperes/cm², (F) in volts/cm, (Φ) in electron volt (eV), and t(y) and f(y) are slowly varying functions their values lie close to unity and are tabulated by many authors (Van Oostrom, 1966; Nordheim, 1928; Gyftopoulos and Levine, 1962; Muller, 1937; Dyke and Dolan, 1956; Burgess *et al.*, 1953; Gadzuk and Plummer, 1973).In experimental field emission work, the emission current (I) in amperes is measured as a function of the applied voltage (V) in volts between the cathode and anode. I and V can be expressed as follows:

$$\mathrm{I} = \mathrm{JA} \rightarrow \mathrm{J} = \frac{\mathrm{I}}{\mathrm{A}} \quad (2)$$

and

$$F = BV \quad (3)$$

where A is the emitting area in cm² and B is called the field factor and has units of cm⁻¹ and its value depends on the geometry of the emitter (Martin *et al.*, 1960). Substituting Eq. (2) and Eq. (3) in Eq. (1) yields

$$\frac{I}{A} = \frac{1.54x10^{-6}B^2V^2}{\emptyset\, t_y^2}\exp\left(-6.83x10^7\frac{\emptyset^{\frac{3}{2}}}{BV}f(y)\right) \quad (4)$$

Rearranging Eq. (4), gives

$$\frac{I}{V^2} = \frac{1.54x10^{-6}B^2A}{\emptyset\, t_y^2}exp\left(-6.83x10^7\frac{\emptyset^{\frac{3}{2}}}{BV}f(y)\right) \quad (5)$$

By taking the logarithm of both sides of Eq. (5), we get

$$log\frac{I}{V^2} = log\left(\frac{1.54x10^{-6}B^2A}{\emptyset\, t_y^2}\right) - 2.96x10^7\frac{\emptyset^{\frac{3}{2}}}{BV}f(y) \quad (6)$$

Plotting $\log\frac{\mathrm{I}}{\mathrm{V}^2}$ versus $\frac{1}{\mathrm{V}}$ results in a straight-line graph called Fowler-Nordheim (FN) plot. The slope of this plot (S_F) is given by (Young and Clark, 1966).

$$S_F = \frac{\Delta log\frac{I}{V^2}}{\Delta\frac{1}{V}} = -2.96x10^7\frac{\emptyset^{\frac{3}{2}}}{B}s(y) \quad (7)$$

where s(y) is another slowly varying function whose values also lie close to unity. For the total tip surface Eq. (7) can be written as

$$S_{F_t} = -2.96x10^7\frac{\emptyset_t^{\frac{3}{2}}}{B_t}s(y) \quad (8)$$

and for any hkl plane of the emitter surface

$$S_{F_p} = -2.96x10^7\frac{\emptyset_p^{\frac{3}{2}}}{B_p}s(y) \quad (9)$$

By dividing Eq. (9) by Eq. (8) we get

$$\frac{S_{F_p}}{S_{F_t}} = \left(\frac{\emptyset_p}{\emptyset_t}\right)^{\frac{3}{2}}\cdot\left(\frac{B_t}{B_p}\right) \quad (10)$$

By solving Eq. (10) for $\emptyset_p$ yields

$$\emptyset_p = \emptyset_t\left(\frac{S_{F_P}}{S_{F_t}}\cdot\frac{B_p}{B_t}\right)^{\frac{2}{3}} \quad (11)$$

By assuming B to be constant over the tip surface, Eq. (11) becomes

$$\emptyset_p = \emptyset_t\left(\frac{S_{F_P}}{S_{F_t}}\cdot\right)^{\frac{2}{3}} \quad (12)$$

If $\emptyset_t$ is known from other experiments data, then $\emptyset_p$ can be calculated. For a clean tip used as a field emitter in this work, an average work function $\emptyset_t = 5.27 \pm 0.01$ eV has been used (Michaelson, 1977; Wilson, 1966).

2. The emitter tip assembly

The emitter tip assembly used in the present study is illustrated in Fig. 2. It was made up of a four-wire tungsten-glass press seal. The tungsten rods had diameters of 1mm. To the end of each rod on the tip side, a short 1 mm diameter nickel rod extension was spot-welded. The extensions were used to aid spot welding the fine tungsten wire to the 1mm diameter tungsten rods. A 0.127 mm diameter 99% pure tungsten wire hairpin loop about 25mm in length was spot-welded to the outer electrodes (a and b). A 4 mm length of 0.1346 mm diameter high-purity iridium wire was spot-welded to the top of the loop under a jet of nitrogen gas to avoid oxidation that might happen if the spot welding was carried out in the air (Melmed, 1965). By heating the loop resistively, the tip could be cleaned. Two 0.127 mm diameter tungsten wires, called the potential leads, were spot-welded to the two inner electrodes (c and d). The other ends of those two wires were spot-welded to the loop on each side of the tip. The potential leads were used to measure the voltage developed across the centre section of the loop when a heating current was passed through the other two electrodes.

A cooling jacket (cold finger) surrounded the support rods to cool the tip down to 78 K using liquid nitrogen. Zuber and Ciszewski (Zuber and Ciszewski, 2000) made iridium tips from 0.1 mm diameter wire by electro polishing in 40% water solution of CrO_3 were spot welded to 0.2 mm molybdenum (Mo) heating loop. The sample was heated by manifold flashes in excess of 2500 K.

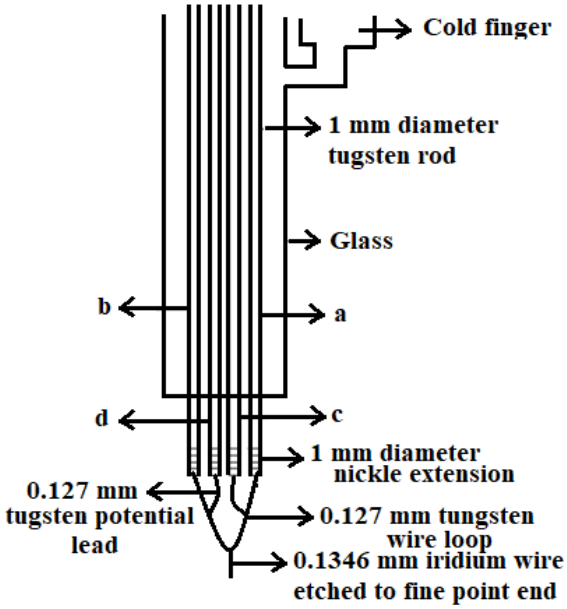

Fig. 2. The emitter tip assembly.

3. The Tip Etching

The face-centered cubic (FCC) metal iridium has been chosen amongst the platinum group metals as a field emitter. Its high melting point (2454°C) (Sinha *et al.*, 1972) together with its low vapour pressure (10^{-8} torr at approximately 1460 °C) allow for suitable cleaning by thermal desorption of impurities. Unlike tungsten, carbon contamination is not a problem with iridium. Iridium points can stand stresses as high as 10^{11} dyne/cm² (Rendulic and Muller, 1966) which means that a high electric field can be applied to the tip without danger of fracture. Emitters of weak materials are subject to fracture under a stress of about 10^9 dyne/cm² (Sinha *et al.*,

1972). The sample of wire used was a 0.0053 inch diameter high purity iridium supplied by Nordiko Ltd. U.K., It was oriented with (100) along the wire axis. A typical clean field emission pattern from iridium emitter with (100) orientation together with the map of the locations of the images of various planes using a tube with a flat fluorescent screen is shown in Fig. 3a and b respectively.

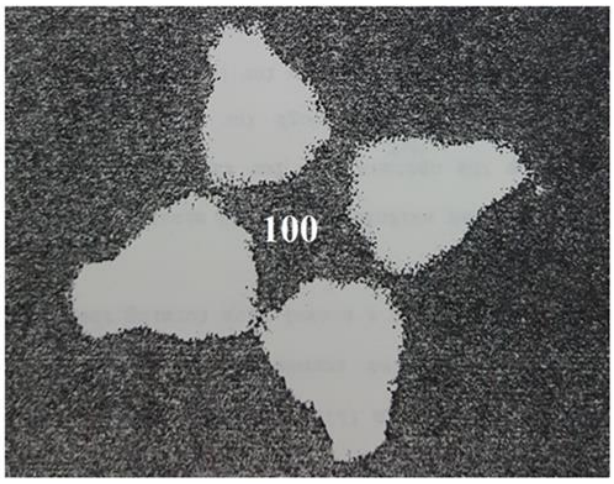

Fig. 3a. Field emission pattern of a clean iridium tip surface.

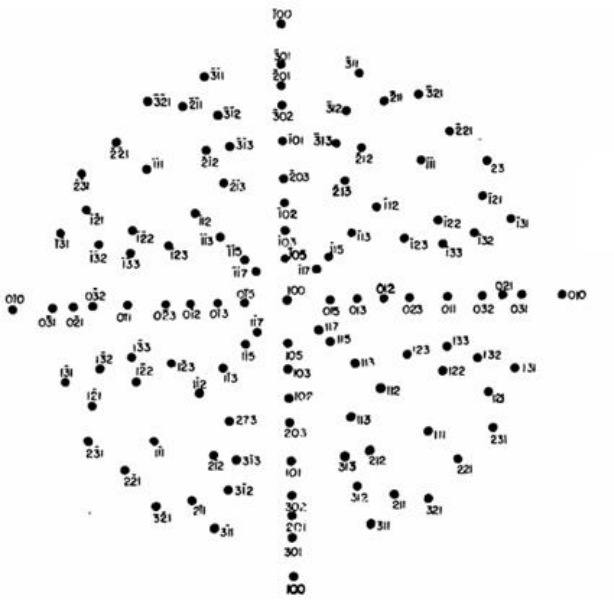

Fig. 3b. A map of location for the images of various planes when using a tube with a flat fluorescent screen.

Different recipes were used to get sharp iridium tips, a 10% KCN solution was used by Brenner (Brenner, 1964), an aqueous 30% CrO_3 solution and AC current between 0.5 amperes and 1.5 amperes by (Nieuwenhuys *et al.*, 1973), a 30% solution of CrO_3 (15 V DC) then a concentrated HNO_3 solution (5 V AC) by (Derochette and Martin, 1977), a molten KOH-$NaHO_3$ mixture by (Rendulic and Muller, 1966), and a molten of 70% KOH, 30% $NaNO_3$ to which some NaCl crystals were added was used by Gorodetskii et.al. (Gorodetskii *et al.*, 1979) and by Witt and Nieuwenhuys (Witt and Nieuwenhuys, 1982).

Recipes for various metals and corresponding etching solutions have been listed by many authors (Muller and Tsong, 1969; Hren and Ranganathan, 1968; Bowkett and Smith, 1970). Lucier (Lucier, 2004) in his M.Sc. thesis explained how to prepare tips of different metals. Moran Meza *et al.*, 2015 showed how to fabricate ultra-sharp platinum/iridium tips which had been reproducibly etched by electro chemical process using an inverse geometry of an electrochemical cell and a dedicated electronic device. Bin and Fritz (Bin and Fritz, 2004) described a method of preparing gold tips by direct current electrochemical etching in concentrated HCl and ethanol solution. They reproducibly prepared gold tips with apex radius lower than 30 nm. Eisele *et al.* (2011) presented a simple method to produce sharp gold tips with excellent surface quality based on electrochemical etching with potassium chloride. Libioulle and Houbion (Libioulle and Houbion, 1995) have developed electrochemical procedures to obtain very sharp platinum and gold tips. The resulting geometry is very reproducible and the mean curvature radius is 5 and 10 nm for the two materials, respectively. Iwami et al. (1998) have used a reliable method to prepare silver tips for scanning procedure based on two–step electrochemical processing; ac electropolishing and subsequent dc electropolishing. The end of the tips were sharpened by field evaporation of silver ions. Ekvall et.al. (Ekvall *et al.*, 1999) have investigated methods for cleaning dc–etched polycrystalline tungsten tips for scanning tunneling microscopy (STM). The cleaning methods included Ar-ion sputtering, heating, chemical treatments and Ne-ion self-sputtering. Ottaviano *et al.*, (2003) have prepared tungsten tips used in scanning tunneling microscopy via electrochemical etching with 2N KOH or NaOH solution. The lateral resolution of the tips was 10 nm. Lindahl *et al.* (1998) have investigated a simple yet powerful method for making sharp tips which were seen by high–resolution transmission electron microscopy to be sharper than 20A^o.

During the present study, two techniques were used to cut the iridium wire electrolytically. Both techniques had pre-etching and final etching stages. In both techniques two etchant solutions were used (1N NaOH and 0.2N NaOH) and two different values of AC voltages (4.5 volts and 6.5 volts) were applied.

In the first technique the iridium specimen was vertically immersed in the 1N NaOH solution as illustrated in Fig. 4, an AC voltage of 4.5 volts was applied across the circuit with iridium specimen forming one electrode and a nickel wire forming the other.

The circuit was switched on for 20 minutes, which after many trials was found to be the optimum time for this stage and resulted in a taper wire, which was not yet sharp enough for the purpose of field emission microscopy. Leaving the specimen for longer time (>20 minutes) resulted in a blunt tip which grew progressively shorter. The specimen was then transferred to a 0.2N NaOH solution. The same circuit illustrated in Fig. 4 was used but with 6.5 volts instead of the 4.5 volts. During this final etching process the specimen was repeatedly immersed, etched for 60 seconds, and examined under a 600x optical microscope until the actual point was not clearly resolvable.

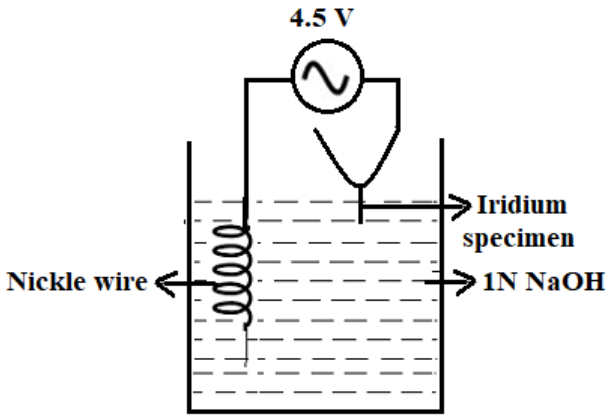

Fig. 4. The circuit for pre-etching iridium wire specimen.

The criteria for a good tip are shortness, smoothness, uniform taper, and an unresolved end. The tip obtained by the method outlined above had most of the mentioned features of a good tip, but it was not short enough, as we could not make it shorter than about 4mm which is not very convenient for field emission studies since high current will be required to pass through the support loop to clean the tip (Dyke and Dolan, 1956).

To avoid that inconvenience another technique called a thin layer technique was used (Muller and Tsong, 1969). In this technique, a thin layer of 1N NaOH solution was floated on carbon tetrachloride, CCl_4, which is immiscible liquid of higher density and does not react with iridium wire, thus limiting the electrochemical attack on the specimen wire to a short section only. The iridium wire was immersed vertically intersecting both the etchant and the supporting liquid. The depth of the etchant and the length of the wire in the etchant were adjusted to limit the final length of the tip to about 1 to 2 mm to ensure sufficiently high temperatures at the tip when passing relatively low currents through the support loop.

A circuit similar to the one depicted in Fig. 5 was set up. The pre-etching process lasted 20 to 30 minutes. After 20 minutes the etching process was closely being monitored and when the part immersed in the 1N NaOH was appreciably thinned, the circuit was switched off to stop further etching and avoid dropping off the lower end as that would lead to a blunt tip. The waisted specimen was then immersed into a 0.2N NaOH solution using the same circuit illustrated in Fig. 4 and etched by applying 6.5 volts. During this stage the specimen was observed continuously until the lower part dropped off at which point the circuit was immediately switched off. Fig. 6 depicts the various stages during the two-stage etching process. At this stage, either a sharp tip was obtained or more frequently a "bulb" was formed at the apex of the tip as illustrated in Fig. 7.

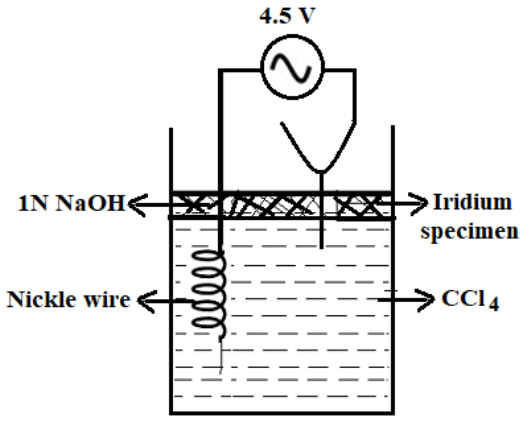

Fig. 5. The arrangement for electropolishing a specimen wire using a thin layer technique.

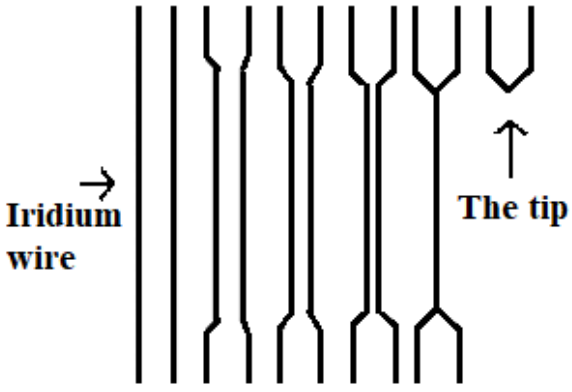

Fig. 6. Various stages during the two-stage etching process used in the thin layer technique (the second etching technique.).

Fig. 7. A bulb at the apex of the tip.

The Size and shape of the bulb were found to be dependent on the length of the dropped end. To get rid of the bulb two methods were used. In the first one the tip was again etched in the 0.2N NaOH. The process being interrupted every 20 seconds to observe the tip under the microscope until a sharp tip was obtained. This method using manually switched AC proved to be difficult because overshoot readily occurred.

To assure controlled removal of the bulb a new circuit was constructed as illustrated in Fig. 8. The suitably charged capacitor (was charged when the switch S is placed at point a in the circuit of Fig. 8.) which was incorporated in the circuit was discharged through the tip wire by shifting the switch (S) to (b) for a very short time. After every discharge, the tip was examined under the microscope. This was repeated until the bulb was removed and a sharp tip was obtained.

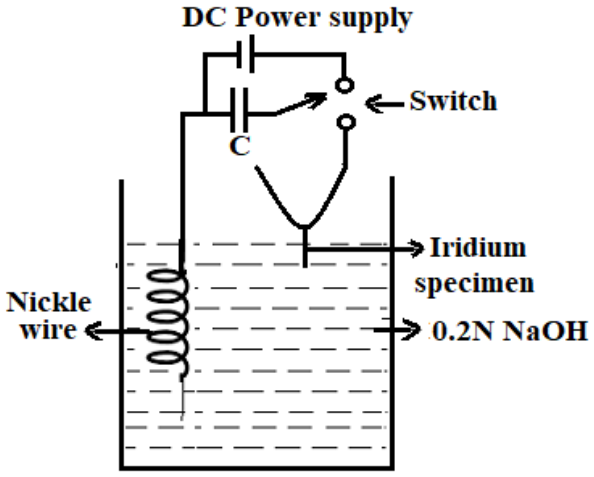

Fig. 8. A capacitor discharge technique through the tip.

The number of the discharges required depends on the size of the bulb and on the value of the capacitor "C". In a power supply routinely used for this purpose, capacitance of 250 microfarads to 2500 microfarads and a voltage up to 15 volts DC could be selected for optimizing the conditions. All etching processes were carried out at room temperature. A number of tips were cut throughout the present work and it was found that using fresh solutions for every tip being etched was essential to achieve good results. Using stale solutions or used ones gave poor results. Washing the tip with tap water or distilled water after it has been etched is an important step to remove the etchant and reaction products sticking to the wire surface.

4. Experimental results and discussion

The iridium used in the present study was (100) oriented. With this orientation, the only well-defined plane which can be studied is the (100), see Fig. 3. This plane is known to be atomically smooth (Ehrlich, 1959; Nieuwenhuys and Sachtler, 1974) and thus having a high work function (Muller, 1955). Due to its high work function, the emitted current from this plane is very low, when a current of 1.5×10^{-6} amperes was drawn from the total tip surface, the current from the 100 plane was of the order of 10^{-13} amperes.

The work function of this plane was measured using Eq. (12) and by assuming the average work function value for iridium to be 5.27 eV (Michaelson, 1977; Wilson, 1966) a value of 6.00±0.02 eV was obtained. This value is higher and does not agree with the value measured by Nieuwenhuys *et al.* (1973) who by taking the average value of the work function of iridium (Φ_{av}) to be 5.00 eV have measured the work function of the (100) plane (Φ_{100}) to be 5.67 eV, but if they had taken (Φ_{av}) to be 5.27 eV, the value adopted in the present study, they would have obtained a value of 5.98 eV for (Φ_{100}) which is very close to 6.00±0.02 eV which we obtained.

Todd and Rhodin (Todd and Rhodin, 1973) and Coles and Jones (Coles and Jones, 1977) have also obtained high work function values for the (110) plane of tungsten and (10$\bar{1}$0) of rhenium respectively and attributed that to the difference in B, the field factor, between the plane under study, B_{hkl}, and the total tip surface, B, which were assumed to be equal when Eq. (12) was used. We may attribute the high value of the (Φ_{100}) to the same cause.

While the measurement of the work function of the 100 plane was being studied a very persistent bright ring in the area of the 100 plane suddenly appeared and could not be removed by thermal cleaning. This is shown in Fig. 9. Many researchers who worked on platinum field emitters and a few on iridium observed the (100) ring and attributed it to different causes.

Komar and Savchenko (Komar and Savchenko, 1962) were able to remove the ring from the platinum surface by a combination of heat treatment and field desorption. It was shown by Melmed (Melmed, 1965) that oxygen stabilizes the (100) ring structure to such an extent that it can no longer be removed by heat treatment, he also stated that the strong emission of the (100) ring is caused by the formation of narrow steps in the (100) vicinal area and results from field enhancement.

Lewis and Gomer (1968) and Gorodestskii *et al.* (1979) reported that the (100) ring of both platinum and iridium was caused by oxygen contamination. Lewis and Gomer (1968) observed that it could be removed by heating to 1200 K for several minutes while Gorodestskii *et al.* (1979) pointed out that the oxygen in the (100) region did not desorb up to 2000 K.

Morgan and Somorjai (1968) and Grant and Hass (1969) concluded that the surface carbon was responsible for the platinum (100) ring. Kojima *et a1*. (1982) attributed the appearance of the (100) ring of platinum to prolonged heating at high temperatures and found that it was difficult to remove.

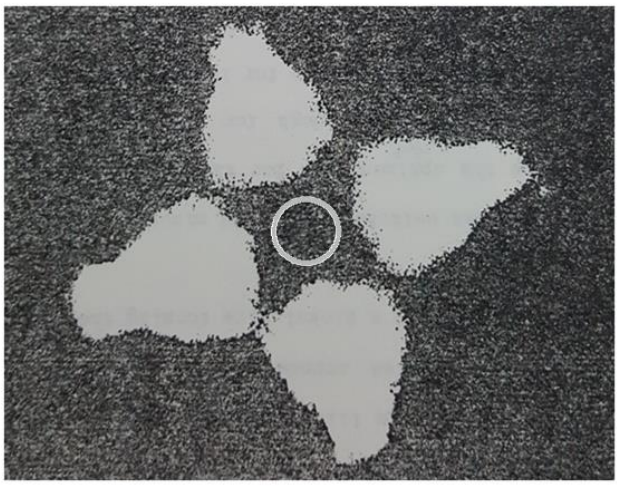

Fig. 9. Field emission pattern of a clean iridium tip surface with the bright ring in the 100 plane.

Mundschau and Vanselow (Mundschau and Vanselow, 1985) reported that the appearance of the ring always occurred after annealing the platinum tip between 870 K and 1500 K and it was attributed to trace amounts of surface carbon and phosphorus. They observed that the ring structure changed in size and shape depending on the annealing temperature and that at high temperature the ring was narrow. In the present study, it was also observed that the size and shape of the iridium (100) ring changed on flashing the tip at different temperatures and to avoid such changes the flashing temperature was kept constant throughout the work on a certain tip. Antczak *et al.* (2000) have also noticed a bright ring around the (100) plane of the iridium tip after annealing the emitter at various temperatures– in particular after intensive heating and flashing the sample to a temperature close to its melting point, and then rapid quenching to room temperature. They attributed the appearance of the ring to the contamination of the sample.

After the appearance of the ring the work function of the 100 plane (Φ_{100}) was again measured using Eq. (12) and it was found to be 5.80±0.02 eV that is lower than the value we obtained in the absence of the ring and is very close to that found by Nieuwenhuys *et al*., 1973) if they had taken Φ to be 5.27 eV instead of 5.00 eV.

Fig. 10 and Fig. 11 show the current profiles across the (100) plane before and after the appearance of the ring respectively. These figures illustrate the approximately parabolic variation of emission current across the (100) plane. This has been attributed to a parabolic decrease in the field (not work function) from the edge to the centre of the (100) plane (Todd and Rhodin, 1973). Fig. 11 shows much wider current profile and higher emitted current. This may be attributed to the bright ring, which contributes significantly to the current of the 100 plane. The same reason may be given for the reduction of the measured work function of the 100 plane (Φ_{100}) in the presence of the ring.

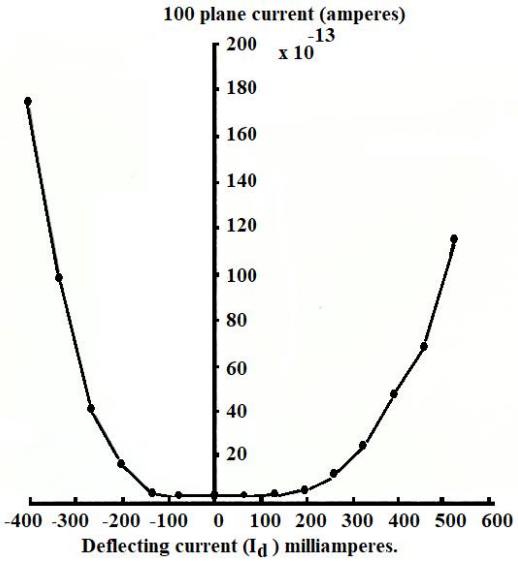

Fig. 10. Current profile across 100 plane in the absence of the ring.

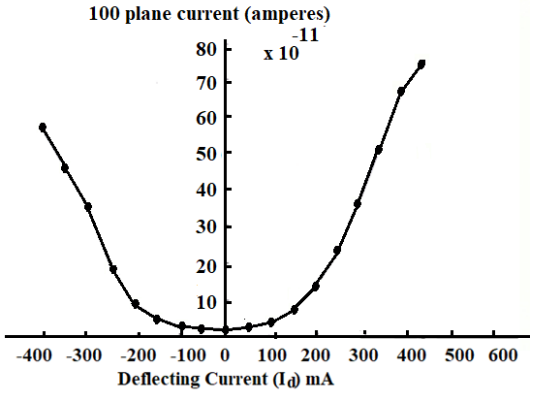

Fig. 11. Current profile across 100 plane in the presence of the ring.

5. Surface Reconstruction of Iridium and Platinum 100 Planes

Hagstrom *et al.* (1965) using the low energy electron diffraction (LEED) technique observed the reconstruction of clean platinum 100 plane after heating in the temperature range 350°C to 550°C for periods from five minutes to five hours depending on the temperature. The surface structure slowly disappears at room temperature but readily reappears when heating to over 400°C (reversible rearrangement), and they consider that these surface structures are the property of clean platinum surface. Grant (1969) has found that, after ion-bombardment and mild annealing of unreconstructed surface, iridium (100) undergoes a reconstruction and gives a sharp (5×1) LEED pattern.

The reconstruction of the platinum 100 plane and that of iridium (100) has been studied by field ion microscopy (Kellogg, 1986) and it was reported that the reconstruction of the iridium (100) occurred above 470K and extended to the second layer atoms. Witt and Muller (Witt and Muller, 1986) have reported that the (1×1) structure of the iridium 100 plane starts to reconstruct into a (5×1) structure at around 900K and the transition is completed at 1200 K to 1300 K. Gas adsorption studies on iridium (100) indicate that the (5x1) structure may be due to oxygen (Grant and Hass, 1969). Biberian (1980) has supposed that the (5×1) structure of iridium (100) is the arrangement adopted by a monolayer of iridium on a (1×1) surface. Grant and Hass (1969) in LEED study have reported that (5×1) and (1×1) diffraction patterns could be formed reversibly from each other after heating at about 700°C or 1200°C respectively for several minutes. These observations do not agree with ours in that the ringed and non-ringed iridium (100) constructions could not be formed optionally, but the occasionally transformation from one structure to the other took place for unknown reasons. The high curvature of the tip surface might possibly favour stabilization of the (5×1) over the (1×1) array.

6. Conclusion

The work function is a fundamental surface property, which can be derived solely from bulk properties and is defined as the minimum energy required to move an electron to the surface of the metal. In this study the work function of the 100 plane (Φ_{100}) of the iridium field emitter (the tip) has been measured using a field emission microscope with a probe hole in the centre of the screen which permitted to examine the individual crystal planes of the tip surface. This plane is known from the ion microscopy to be smooth on atomic scale and it is a dark region because it emits a very small current when a high electric field is used. Two values have been obtained for the (Φ_{100}), one value in the absence of the bright ring 6.00 eV, the other value was measured after the appearance of the bright ring in 100 plane and was found to be 5.98 eV. The (100) ring on the iridium tip surface is believed not to be due to any kind of contamination, but it is another more stable structure for the clean iridium surface.

In spite of the fact that only LEED can give a solution of a structure, it is possible to give here an argument that the ringed (100) structure observed for iridium in the present study cannot be linked to any kind of contamination and we think that the clean surface of iridium has two different structures. The first one which has no ring in the (100) area, and is referred to by the others as the clean, is not very stable and under certain unknown conditions this structure transforms to an alternative structure which forms the ring in the (100) area and seems to be more stable than the first structure. The non-ringed structure may be the (1×1) whereas the ringed structure might be the (5×1).

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