The Photoelectric Properties of the (100) and (111) Faces of a Single Copper Crystal

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The two faces were cut from the same single crystal, and etched to remove the broken surface pieces and to expose only crystal facets which were parallel to the geometric boundaries in question. Care was taken to prevent any contacts between the prepared planes and foreign objects. The two specimens were heated simultaneously by electronic bombardment at various red-heat temperatures for over 1500 hours in a good vacuum. The photoelectric thresholds were measured by the use of filters as the outgassing proceeded. During readings, the pressure was less than 5×10^{-8} mm Hg. After 500 hours of outgassing the threshold wavelengths were approximately 2540A for the (111) face and 2200A for the (100) face. The results show that the etching produced by evaporation should be avoided in such an experiment.

INTRODUCTION

THIS experiment was undertaken as a part of a rather extended series of investigations concerning the properties of single metallic crystals instituted at Brown University several years ago. The main work has of course been Dr. Farnsworth's investigations on electron diffraction. M. L. Williams[1] has reported on soft x-rays from copper crystals, and B. A. Rose[2] has published an account of his work on the contact difference of potential. The purpose of this experiment is to investigate the photoelectric properties of the (100) and the (111) faces of a single copper crystal.

The experiments of Goetz,[3] Cardwell,[4] Linder,[5] Dillon,[6] Nitzsche[7] and others have indicated the influence of crystal structure on photoelectric phenomena. The work of Nitzsche is the first in which the photoelectric thresholds have been measured for more than one distinctly prepared crystal face of the same single crystal. However, no attempt was made to remove occluded gases by heating in a good vacuum, and contaminating vapors were present.

PREPARATION OF CRYSTALS

Two pieces were cut from a large single copper crystal in such a manner that a geometrical face of one was parallel to a (100) set of planes and that of the other parallel to a (111) set of planes. The method of accomplishing this is described in detail by Dr. Farnsworth.[8] The surfaces were smoothed on stones, and the final grinding was done on plate glass with a very fine grinding compound. The final grinding was considerably speeded up by using a dilute solution of nitric acid (about 5 percent) as a lubricant instead of water.

After the surfaces were made as scratch free as possible they were given a final etching. The (111) face was exposed by electrolysis in a copper sulphate solution (30 ma at 0.8 volt for 3 hours). It is important to have the electrode plane and parallel to the crystal face. This method gives an exceptionally good crystal face, very few reflections from other planes being visible. The preparation of the (100) face presented considerable difficulty. It was found best to use a preliminary etching bath consisting of a 55 percent (by volume) solution of nitric acid at 25°C until all of the broken crystals were removed and a smooth matte surface was secured. The face was then finally etched in a 64 percent solution of nitric acid at 27°C. The concentration required varies with the temperature. It is highly important to keep the face wet. If it becomes dry when it is taken out for inspection, it must not be put back into the strong solution until it is first wetted in the weaker one; otherwise, a streaked surface will result. If the acid is too strong a reddish brown surface is formed; if it is too weak the surface has a silky appearance. Once a good surface was obtained care was taken to prevent anything from touching it. As soon

[1] Williams, Phys. Rev. **44**, 610 (1933).
[2] Rose, Phys. Rev. **44**, 585 (1933).
[3] Goetz, Phys. Rev. **33**, 373 (1929).
[4] Cardwell, Proc. Nat. Acad. Sci. **14**, 439 (1928).
[5] Linder, Phys. Rev. **30**, 649 (1927).
[6] Dillon, Phys. Rev. **38**, 408 (1931).
[7] Nitzsche, Ann. d. Physik **5**, 14, 463 (1932).
[8] Farnsworth, Phys. Rev. **34**, 683 (1929).

as practical after giving the crystals a final cleaning in a cyanide solution and then distilled water, they were placed in the experimental tube which was quickly evacuated.

Experimental Tube

The mountings of the crystals were designed so as to minimize illumination by stray light, to prevent recrystallization at the crystal faces and to reduce to a minimum the amount of metal containing occluded gases. The first condition is primarily a matter of geometry. In order to realize the second requirement, the point of mechanical contact with the crystal was placed as far away from the front face as possible and the crystal was backed with molybdenum, since direct electronic bombardment causes recrystallization. The third condition was fulfilled by making the movable parts almost entirely out of glass. The mechanical arrangement was such that the two faces could be alternately moved in front of a quartz window, and could also be moved into position for heating by electronic bombardment. The motion was accomplished by external electromagnets acting on iron armatures inside the vacuum. These armatures were completely enclosed in snug fitting vacuum-tight glass tubes, thus eliminating a large source of gas. The whole assembly fitted into the containing tube, the walls of which were the bearing surfaces. A glass guide was introduced which accurately determined the position of the crystals when they were moved into their different locations. The only exposed metal parts, except the crystals, were the two supporting wires, two very thin shields (not shown) and the anode, all of which were made of molybdenum. The scale drawing in Fig. 1 shows the constructional details.

Procedure and Results

The experimental tube was attached to a two-stage diffusion pump vacuum system, and the trap between the last oil diffusion pump and the experimental tube was cooled by solid carbon dioxide in acetone. The vapor pumps were kept running continuously throughout the experiment. After baking the tube for about 36 hours at 400°C the filaments were given a short outgassing at red-heat temperatures, the exposed glass parts were torched, and the carbon dioxide refrigerant was then removed from the trap. After 10 minutes the lower end of the trap was surrounded by carbon dioxide snow for an additional 15 minutes. This allowed the inside walls to warm up so that the water vapor and other condensed gases were pumped out, and at the same time oil vapor was kept from contaminating the experimental tube. The Dewar flask containing the cooling agent was then immediately replaced. The exposed glass parts were again torched and the baking process continued for another 48 hours. Under the best conditions the pressure was about 1×10^{-8} mm Hg as read on an ionization gauge. After the filaments were sufficiently outgassed the crystals were heated by electronic bombardment. The ionization gauge was kept running continuously during the early stages of heating, and the power input was adjusted so that the pressure was kept below 10^{-5} mm Hg and usually nearer 10^{-6} mm Hg. It required several hours of cautious heating to bring the crystals up to a very dull red heat without any unduly high pressure surges. The heatings were continued at dull red heat for 550 hours before any noticeable evaporation appeared. The deposit from evaporation became appreciable after the 875th hour of heating. The two crystals were outgassed simultaneously for over 1500 hours.

A quartz mercury arc was used as a source of light in conjunction with a set of liquid light filters, which were checked at frequent intervals by photographing the mercury spectrum when the different ones were placed in front of the slit of a Hilger quartz spectrograph. The photocurrents were measured by means of a Soller[9] amplifier whose maximum sensitivity was 2×10^{-15} amp./mm.

The experimental data were obtained by measuring successively the photo-currents from the two crystal faces when the various filters were placed in front of the quartz window. Although this procedure does not permit an application of Fowler's[10] method for a precise determination of the long wavelength limits, it should reveal any differences in the photoelectric

[9] Soller, Rev. Sci. Inst. **3**, 416 (1932).
[10] Fowler, Phys. Rev. **38**, 45 (1931).

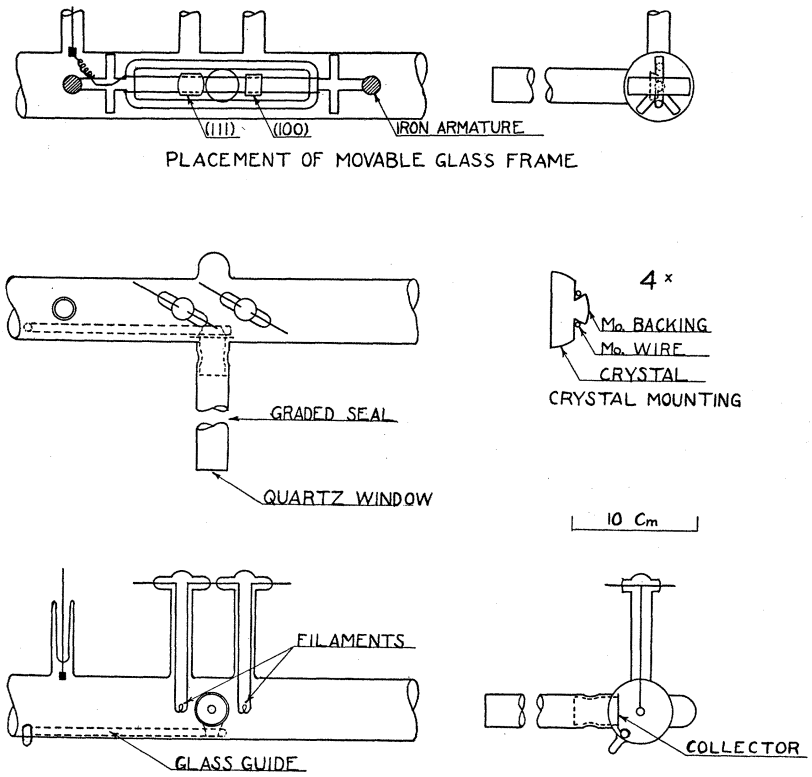

Fig. 1. Experimental tube.

characteristics of the two faces. These currents were plotted against the filter number. An inspection of all the curves shows that the greatest difference in the work function for the two faces appeared after about the 500th hour of accumulated heat treatment. This difference is shown by the graph in Fig. 2. The marked points are believed to indicate the true difference between the two faces which at this stage of the outgassing amounts to approximately 0.73 volt. The surface work function is readily obtained in volts from the relationship $\phi = 12{,}336/\lambda$ (λ expressed in A) and a knowledge of the short wave cut-offs of the filters. The lower horizontal portion at the bottom of the (100) graph has been ignored and ascribed to the presence of foreign crystal planes. The assumption that the small currents represented by this portion of the (100) curves are due to the presence of contaminating facets is supported by the appearance of the curves after evaporation had taken place. After evaporation became appreciable at about the 875th hour of heating, these currents were greatly increased in magnitude. One should expect that the face with the larger work function would be affected most by the contaminating facets, and that as the contamination increased the curves would come to represent the photoelectric characteristics of the plane of smallest work function rather than the characteristics of the prepared faces. This is what was observed. As the heatings were continued at temperatures high enough to produce evaporation, the curves for the two faces became more and more alike, so that finally they were barely distinguishable and the thresholds were extended to about 2536–2650A. An examination of a carefully prepared crystal plane before and after evaporation shows quite definitely that the evaporation process does expose other planes. In order to be sure that the difference observed between the two faces was not due to different outgassing rates, the

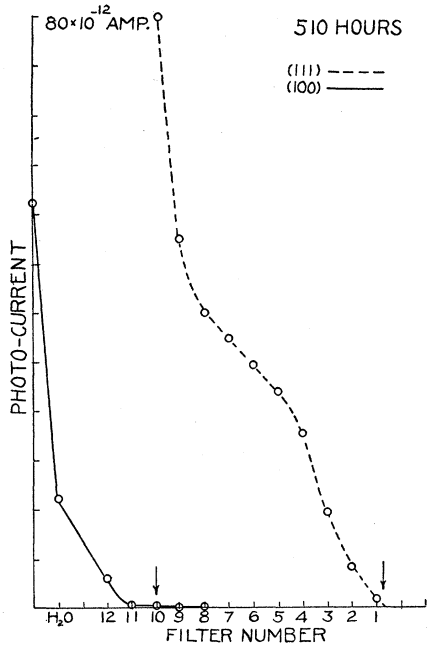

FIG. 2. Photo-current *vs.* filter number for the (111) and (100) faces.

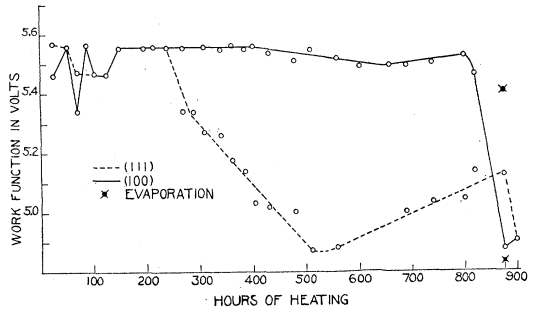

FIG. 3. Work function in volts *vs.* hours of heating for the (111) and (100) faces.

outgassing was occasionally carried out with one of the crystals at a higher temperature than the other. This deliberate heating of either crystal at a higher temperature did not cause the graphs to reverse their relative positions.

All of the curves of the type shown for the 510th hour (Fig. 2) were examined and the work functions of the two faces estimated from them. These estimated work functions are plotted with the corresponding hours of accumulated heat treatment in Fig. 3. An inspection of this graph shows the dependence of the work function on the crystal plane and on the hours of outgassing. The great influence of surface conditions is well exemplified. The problem of obtaining a clean gas free surface is one of the major difficulties encountered in any photoelectric experiment designed to reveal the intrinsic properties of the given substance.

CONCLUSION

The evaporation of metal from the surface constitutes a form of etching. Hence, the outgassing of a single crystal must be carried out at temperatures low enough to prevent evaporation if the original face is to be preserved.

The (111) face assumed a maximum value of approximately 0.73 volt positive with respect to the (100) face after 500 hours of outgassing. This difference is greater than the maximum difference reported by B. A. Rose[2] in his investigation of the contact difference of potential and is of the same sign. The corresponding threshold wavelengths are 2540A for the (111) and 2200A for the (100) faces. The work is being continued with a monochromatic illuminator.

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I wish to express my sincere appreciation of the kind supervision and help which Dr. Farnsworth so freely gave. His help and friendly consideration in times of difficulty enabled me to continue. I am indebted to Mr. H. E. Darling for continuing the readings after circumstance made it necessary for me to leave before the outgassing procedure was completed. This work was done while the author was a recipient of a Brown University Fellowship.