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## PHOTOEFFECT ON CU ANODE DURING ELECTROPOLISHING

The photoelectrical properties of the rotating Cu disc electrode have been investigated.

It has been polarized anodically in 65% orto-H\_PO4.

Presence of the oxide layer on the electrode surface has been stated. The layer has n - semiconductor properties at high values of anodic potential of polarization.

#### INTRODUCTION

Most metals can be polished electrochemically. With copper, this can be achieved in concentrated orthophosphoric acid [1-4]. Many studies have been devoted to the Cu/H<sub>3</sub>PO<sub>4</sub> system and various models of the interfacial anodic process have been suggested, depending largely on the properties studied and on the experimental conditions. In situ measurements were recently attempted [5], one such technique is to excite the anode surface with light and to study the photoresponse [6], which is expected to give information on the nature of the surface and its changes during polishing.

In this paper we study some properties of the  $Cu/H_3PO_4$  system, such as the dependence of its photoeffect on the potential and rotation speed of the anode.

#### EXPERIMENTAL

The apparatus used to study the photoeffect of the system is shown in Fig. 1.

Optical system: The light source is a high-pressure Xe-450 X lamp. Its beam crosses successively an object condenser, a shutter

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Fig. 1. Schematic representation of the apparatus: LS - light source, O - object condenser, Ch - chopper, M - mirror, L - lens, QW - quartz window, C - cell, A - copper anode, 'PS - potentiostat, FG - function generator, LA - lock-in-amplifier

or chopper, which determines the illumination time, a reflecting mirror, a focusing lens and a quartz window at the bottom of the cell. The electrolyte used in our experiments was 60% orthophosphoric acid. The surface of the anode was mechanically polished and rinsed with distilled water before the measurements. The potential was controlled with a potentiostat (AFKEL 419A) and when the light chopper was used the photocurrent was measured with a lock-in-amplifier (PAR 129A). A sweep generator (EMG TR-0455) was applied for the linear sweep experiments.

#### RESULTS AND DISCUSSION

# Dark current experiments

Some characteristic curves are shown in Fig. 2 for different rotation speeds ( $\omega$ ) of the anode. As the potential is increased, the current rises up to a maximum. At higher potentials, the current







begins to decrease, passes through an oscillating zone, and attains a steady-state limit. The polishing process occurs on the current plateau. The current on the polishing level rises as the rotation speed of the anode is increased. The plot of the limiting current vs.  $\omega^{1/2}$  is linear, i.e. the limiting process occurs mainly by diffusion on the solution side of the surface layer.

## Photoeffect

Figure 3 shows a typical photoresponse to a 1 s flash of white light. The photocurrent is positive in the whole range of potential and displays a dual character. At the moment the light is switched on, the current changes rapidly (a) and this is followed by a slower change (b). The rise in current in section (b) is proportional to the duration of illumination. The ratio of the rapid and slow changes depends on the potential and the rotation speed of the anode.

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Through decrease of the duration of illumination, the slow component may be decreased and may thereby be separated from the rapid component. Satisfactory separation could be achieved by applying a fairly large chopper frequency, of around 20 Hz.

### Dependence of the photoresponse on the potential

Figure 4 illustrates measurements with a light chopper frequency of 22 Hz. The photoeffect can be detected only at a rather large anodic potential. This effect increases as the potential increases up to the zone of oscillation. After the oscillation there is a special character in the change of the photocurrent. The response decreases very rapidly as the potential increases, and passes through a minimum and a maximum before reaching a steady state. Change of the rotation speed of the anode leads to a similar curve to those in Fig. 2, but shifted.

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Fig. 4. Photocurrent-potential curves at 1050 and 750 rpm rotation speed of the anode. Chopper frequency was 22 Hz

## Conclusions

Our photoeffect studies on a Cu anode during electropolishing in  $H_3PO_4$  solution provide evidence of the existence of a semiconductor oxide layer on the surface. Due to the positive photoresponse in the whole potential range, this layer is an n-type semiconductor. The photoeffect observed in the polishing plateau suggests changes in the structure of the oxide layer, although the dark current does not change.

The similarity of the photocurrent vs. potential curves at different rotation speeds suggests that the changes in the structure of the oxide layer are independent of the dark current.

A better understanding of the character of the photocurrent--potential curves and the assumed changes in the structure of the oxide requires further studies.

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## FOTOEFEKTY NA ANODZIE Cu PODCZAS ELEKTROCHEMICZNEGO POLEROWANIA

Zbadano fotoelektryczne właściwości powierzchni wirującej dyskowej elektrody miedzianej polaryzowanej anodowo w 65% kwasie ortofosforowym.

Na powierzchni elektrody stwierdzono obecność warstwy tlenkowej o właściwościach n-półprzewodnika w wysokich wartościach anodowego potencjału polaryzacji.