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Evaluation of semiconductive properties of the oxide films on copper

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Photocurrent/photovoltage has become an important tool in the investigation of passive films. The photovoltages were measured for copper in sodium hydroxide using a high power light source for different durations. The film growth is logarithmic in nature and exhibits positive photopotential as light is shone on them. The auto power of electrochemical noise was measured both in dark and illuminated conditions. Band gap of the film was calculated from the absorption spectrum.

Key words: Copper, photo potential, auto power, passive film

INTRODUCTION

In recent times, much attention has been focused on characterising the electronic properties of passive films formed on metals and alloys by photoelectrochemical techniques [1]. Depending upon the properties of the passive films with respect to its conduction type, different energetic conditions can be distinguished.

Evaluation of semiconductor parameters like band gap, concentration of charge carrier, flat band potential etc. will give some idea about the metal/oxide/electrolyte interfaces which in turn will give more details about the passive films. Also the thickness of the film formed on the transition metals are going to be intermediate than compared to noble or valve metals and nonstoichimetric in composition. Hence their properties will very much get affected with time by the applied potentials and also on irradiation. Evaluation of some of these parameters will help in understanding the extent of involvement of these oxide films in corrosion processes.

In the present investigation, an attempt has been made to evaluate the characteristic of the film formed on copper in weak alkaline solutions. The electrochemical noise measurements have also been carried out to study the film growth mechanism.

EXPERIMENTAL

Two identical copper electrodes of high purity polished to a mirror finish, degreased with trichloroethylene and lacquered, to get a geometrical area of 1 sq. cm were exposed to the medium. A PVC cell consisting of two compartments separated by a thin perforated PVC sheet was used in such a way that one of the two specimens can be irradiated.

A high pressure Hg/Xe light source was used to illuminate the electrode surface. Solution of AR grade sodium hydroxide was used. The electrochemical noise measurements were carried out using 1200 Signal Processor (Solartron, UK) [2]. A double beam UV 3400 Spectrophotometer (Hitachi, Japan) was used to obtain absorption spectrum of oxide films. The photopotentials were measured for every one hour.

RESULTS AND DISCUSSION

The photopotential for the passive film formed on copper in 0.1N NaOH is found to be positive and it grows logarithmically with time [3].

Figure 1 shows the corrected absorption spectrum of passive film formed on copper in 0.1N NaOH for various time intervals. The absorption peak at 480 nm after 6th hr. is more pronounced than those obtained after 1st and 3rd hours indicating the presence of stable cuprous oxide with band gap of 2.13 eV.

Table I gives the influence of irradiation on the auto power of noise spectrum (200 mHz –10 Hz) for copper in 0.1N NaOH solution. These data show that in dark, not only the noise power is low but also the changes are very small. On illumination, there is an increase of noise power with time. Generally, the film formed is going to be very thin and amorphous in nature [4]. Further, the growth of the film is enhanced by the transport of metal cations to the oxide/electrolyte interface through the defects in the oxide film. However in dark the increase in carrier

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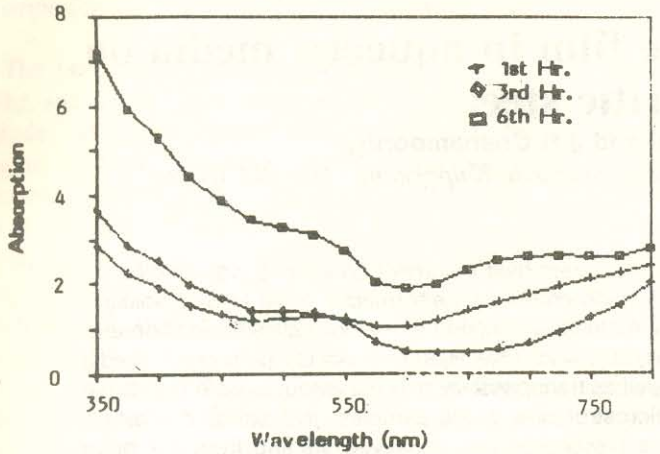

Fig. 1: Absorption spectrum

concentration on the film is negligible even though the thickness of the film increases with time. On illumination, nonequilibrium electrons and holes are formed and the carrier concentration at the surface increases leading to the acceleration of the electrode reaction. As the film grows, it will absorb more light generating electron-hole pairs which lead to the increase in noise power.

CONCLUSION

The oxide formed on copper in alkaline medium exhibits a positive photopotential and its growth is logarithmic with time. The absorption spectrum indicates the existence of mixed oxides of copper after 3rd hour of exposure and the band gap measured lies in the range of 2.13eV.

TABLE–I

Hours	Autopower	
	Dark	Light
1	1.8726e–11	6.2132e–8
2	2.0736e–11	8.8921e–8
3	2.2009e–11	1.2805e-10
4	1.4915e–11	8.8278e-10
5	1.0959e–11	1.1641e–8
10	6.6937e–11	9.7231e–8
15	6.9848e–11	1.4041e–6

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