PHOTOVOLTAIC STUDY OF ANODICALLY GROWN OXIDE FILMS ON Ag–Cu ALLOYS

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Semiconducting oxide films grown by anodic oxidation on Ag–Cu alloys were studied by using the photovoltaic effect at the oxide film–metallic substrate interface. Single-phase metallic alloys yielded single-phase oxides, while samples of two or three Ag–Cu metallic phases yielded more than one oxide phase. The composition and stability of the semiconducting oxide films were influenced by the nature of the oxidizing solution as much as by the composition of the metallic alloy they were grown from, as evidenced by the energy gaps measured from the photovoltaic spectra and the X-ray powder diffraction analysis.

1. INTRODUCTION

Cu_2O [1] and Ag_2O [2] films have previously been grown anodically and studied by using the photovoltaic effect. Since both oxides have the same crystalline structure [3], there is an interesting possibility of growing a substitutional type of Ag–Cu mixed oxide. Thermal oxidation of copper followed by doping with silver concentrations up to 2 at.% in Cu_2O was carried out by Schwab and coworkers [4,5]. Hayashi and Ogawa [6] also thermally oxidized Ag–Cu alloys, with a silver concentration in the grown oxide again of no more than 2 at.%. The above groups studied the influence of a small amount of silver doping in the excitonic structure of Cu_2O by absorption measurements at low temperature. It is clear from the above studies that one cannot have a high concentration of silver substitutionally in Cu_2O or of copper in Ag_2O since Ag_2O itself is unstable [7] at $T = 160\,^{\circ}C$ at atmospheric pressure. Therefore, thermally it is not likely to be possible to obtain a mixed oxide.

Anodic oxidation, being a relatively low temperature oxidation process, may thus be the only possible way that one could grow a mixed oxide ($Ag_{2x}Cu_{2(1-x)}O$) with a large concentration of silver. The metallic alloys used here were rapidly quenched from the melt in the hope of obtaining a single or metastable phase, and thus a single-phase mixed oxide. Micrometre-thick oxide films were grown on the metallic alloy substrate by using a variety of solutions. The films were characterized by X-ray powder diffraction and by studying their photovoltaic spectra at room temperature.

2. EXPERIMENTAL DETAILS

2.1. Metallic alloy preparation

Ag–Cu alloys (the phase diagram can be found in ref. 8) of various concentrations were prepared by melting silver and copper at 99.99 at.% purity in an argon or a nitrogen atmosphere at 1100 °C inside a sealed quartz tube. The molten metallic alloys were rapidly cooled by submerging the quartz tube in water. Thin rectangular metallic samples were prepared for oxidation by the following procedure: (a) rolling down the alloy pellet; (b) polishing mechanically with increasingly finer powders; (c) etching chemically in H_2O_2:NH_4OH (1:4 parts); (d) cleaning with distilled water in an ultrasonic bath.

The alloys were analysed by X-ray diffraction, which indicated that for concentrations of silver and copper up to 8 at.% a single-phase metastable alloy was obtained[8]. A two-phase system (silver and copper phases) was usually obtained if the concentration of one of the alloy components was higher than 8 at.%. For one of the prepared metallic alloys (37 at.% Ag–63 at.% Cu) there were indications of a third crystalline phase (metastable Ag–Cu phase): as evidenced by X-ray diffraction, the lattice parameter of the metastable phase was 3.75 ± 0.01 Å, corresponding to 25 at.% Ag–75 at.% Cu [9].

2.2. Oxidation

The oxidizing solutions and current, voltage and temperature conditions followed were those that were previously found to grow relatively good quality micrometre-thick Cu_2O [1] and Ag_2O [2] films.

(S1) 0.01 M $CuSO_4$ + 0.005 M NaCl + 0.005 M LiCl (pH about 5.2). Oxidizing conditions: constant current, 20–30 A m^{-2}; $t = 1$–2 h; $T = 80$–85 °C.

(S2) 0.02 M Ag_2SO_4 + 0.17 M NH_4OH (pH about 11.8). Oxidizing conditions: constant current, 30–40 A m^{-2}; $t = 2$–3 h; $T = 25$–45 °C; slow stirring.

(S3) 2 M NaOH (pH about 12.2). Oxidizing conditions: constant current, 2–3 A m^{-2}, or constant voltage, 0.20–0.25 V; $t = 3$–4 h; $T = 40$–45 °C; fast stirring.

Solution (S1) favours Cu_2O growth while solutions (S2) and (S3) favour Ag_2O. All solutions were prepared using reagent-grade chemicals and distilled water and were saturated with both Ag_2O and Cu_2O powders during oxidation to avoid dissolution of any of the oxides grown.

A major difficulty is that there are no conditions in the potential–pH diagrams of the Ag, Cu–H_2O systems[10] that would favour equally well the growth of Ag_2O and Cu_2O. These potential–pH diagrams, however, are only valid for solution (S3). The particular composition of solutions (S1) and (S2) and the as-yet unknown film formation mechanisms associated with them may possibly allow mixed oxide growth.

2.3. Characterization of the oxide films

The oxides were examined by X-ray diffraction of powder samples scraped off the films to reveal the nature of their constituents. The characteristics of several samples of various Ag–Cu concentrations, oxidized in the three solutions available, are presented in Table I. In general, whenever the metallic alloy was two phase and

TABLE I

GENERAL CHARACTERISTICS OF SAMPLES

Sample number	Solution	Composition of metallic alloy Ag–Cu (at.%)	Predominant oxide(s) grown	Photovoltage (500 W m⁻²) (mV)	Energy gap (eV)	Comments
1	(S2)	100–0, SP	Ag_2O	100	1.42 ± 0.03	Ref. 2
2	(S2)	96.5–3.5, SP	Mixed oxide, AgO	0.11	1.52 ± 0.05	
3	(S3)	96.5–3.5, SP	Mixed oxide, AgO	0.10	1.61 ± 0.05	
4	(S1)	91.5–8.5, SP	Mixed oxide	100	1.85 ± 0.03	Photomemory effects
5	(S1)	37–63[a], TP 27–75[b]	Cu_2O, mixed oxide	130	2.02 ± 0.03 1.80 ± 0.10	Traces of AgCl, Ag, AgO
6	(S2)	37–63[a], TP 25–75[b]	Ag_2O	—	—	Cu phase not oxidized
7	(S3)	37–63[a], TP 25–75[b]	Ag_2O	0.15	—	Cu phase covered by thin oxide
8	(S1)	17–83, DP	Cu_2O, AgO	1.2	2.02 ± 0.03	Traces of AgCl
9	(S1)	1–99, SP	Cu_2O	220	2.00 ± 0.03	
10	(S1)	0–100, SP	Cu_2O	250	2.02 ± 0.03	Ref. 1

SP, single phase; DP, double phase; TP, triple phase.
[a]Composition as before alloying.
[b]Composition of metastable phase[9].

oxidized in a solution favouring either Ag_2O or Cu_2O, the oxide predominantly grown was that favoured by the solution. A mixed oxide was usually obtained when the metallic alloy was single phase. There was evidence that compounds from the solution were incorporated in small amounts in the oxide during oxidation. Several samples showed the presence of AgO and AgCl at the same time, particularly for those metallic alloys oxidized in solution (S1).

Examination with an optical microscope revealed that all two- and three-phase metallic alloy samples were totally covered by an oxide film when oxidized in solution (S1). With solutions (S2) and (S3) oxide coverage was complete only on the silver phase, while the copper phase was only covered by a very thin film: these almost bare regions (usually 5–10 μm in diameter and a few tenths of a nanometre thick) acted as electrical shorting paths preventing any electrical measurements (samples 6 and 7, Table I). The single-phase metallic alloys were always covered by an oxide film in all three solutions.

2.4. Photovoltaic spectra

A gold film 7–8 nm thick was evaporated onto the oxide film surface to serve as an ohmic semitransparent contact for the photovoltaic measurements. Figure 1 shows the sample configuration with respect to the incident light. The magnitude of the photovoltage obtained by illumination with a quartz–iodine lamp (intensity of 500 W m⁻² on the sample surface), suggested to a certain extent the structural quality of the oxides grown. The lower the photovoltage (Table I), the larger the

number of defects and low resistance paths in the oxide film. The samples that exhibited rectification were usually a few micrometres thick, varying locally owing to the relief of the pyramidal polycrystalline texture.
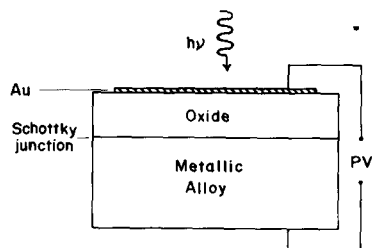
Fig. 1. Sample configuration for photovoltaic measurements.

The photoresponse spectra of the metallic alloy–oxide junction were taken using chopped radiation from a Bausch–Lomb high intensity monochromator with a 12 nm bandwidth. The photosignal was detected with a phase-sensitive amplifier, thus avoiding charging effects[1] associated with d.c. measurements. The energy gaps were deduced from the photovoltaic spectra using the Moss criterion[11] and they were indicative of the nature of the oxides grown. The polarity of the photosignal, when compared with that of either Ag_2O [2,12,13] or Cu_2O [14], which are known to be p-type semiconductors, indicated that all grown oxide samples were p type.

In Fig. 2, a number of photovoltaic spectra are presented which show a representative change in response for the various samples (the number attributed to each curve corresponds to the same sample number in Table I) as one moves from
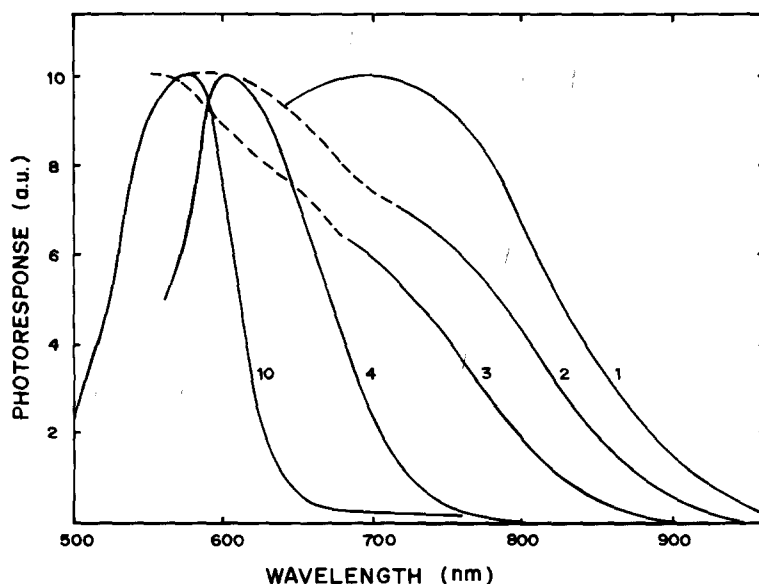
Fig. 2. Normalized photoresponse spectra for various oxide films. The sample numbers are as in Table I.

Cu_2O (curve 10) to Ag_2O (curve 1). The broken line section of the photoresponse curves 2 and 3 is due to the presence of AgO ($E_g \approx 2.2$ eV) in the grown oxide films as was indicated by X-ray powder diffraction.

Figure 3 illustrates the energy gap variation of the various grown oxide films as a function of the copper atomic percentage in the metallic alloy they were grown from.
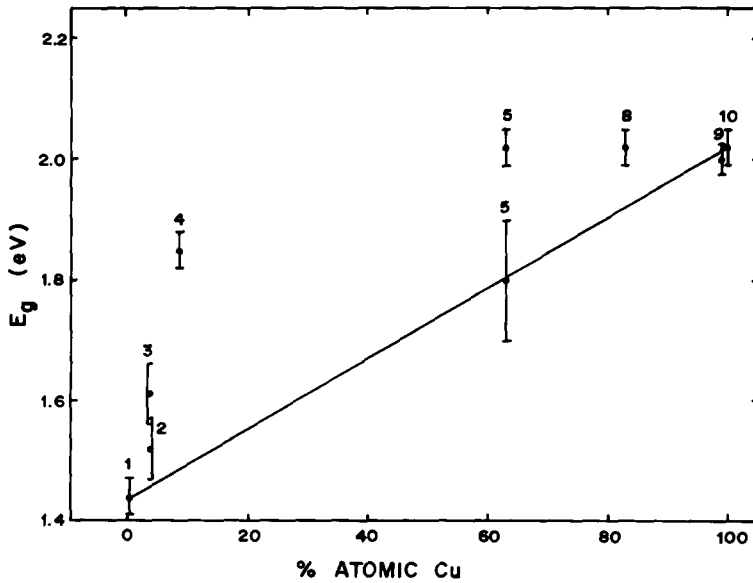

Fig. 3. Energy gap of the oxide films as a function of the metallic alloy composition. The sample numbers are as in Table I.

It should be noted that for sample 5 two energy gap values are presented. The evidence for these values comes from the photovoltaic spectrum. It showed a typical Cu_2O photoresponse curve plus a second curve of reverse polarity at longer wavelengths: that second curve could be attributed to a second phase in the sample, possibly a mixed Ag–Cu oxide, as the band gap value suggests. When a photovoltaic spectrum was obtained from the same sample a week later, the second curve was missing, indicating that the mixed oxide was in fact unstable. The error bars of the energy gap are determined by both the scatter in the data and the accuracy of the method they were determined from (Moss criterion).

The solid line between the energy gaps of pure Ag_2O and Cu_2O represents the suggested theoretical energy gap variation, assuming that (a) both silver and copper are readily oxidized without any preference towards one or the other by the solutions used and (b) silver and copper are interchangeable in the mixed oxide lattice. It is evident from Fig. 3 that there is always more copper in the oxide grown than expected from the existing copper concentration in the metallic alloy, suggesting that copper is more easily oxidized than silver.

3. DISCUSSION

Considering the difference in chemical stability between Cu_2O and Ag_2O, one could obtain a tentative explanation of certain of the observed phenomena. For copper and its oxides in air, CuO is the most stable followed by Cu_2O and copper. In the case of the silver oxides–air system the opposite order is valid, *i.e.* silver is the most stable followed by Ag_2O and AgO. Therefore an Ag–Cu mixed oxide would tend to dissociate into CuO and silver. However, the dissociation of Cu_2O to CuO is a very slow process at room temperature; thus Cu_2O together with silver are more likely to be the dissociation products of the mixed oxide. In turn, the reduced silver in the oxide creates low resistance paths, "killing" the photovoltaic response. This is generally the case for oxides grown with solution (S1) as evidenced by X-ray powder diffraction. Solutions (S2) and (S3) seem to grow more stable oxides on a silver-rich single-phase metallic alloy.

It is also worth mentioning that photomemory and photosignal evolution effects have been observed here; as they have been previously for anodically oxidized copper[1] and silver[2]. This may also be a result of structural and compositional changes with time in the alloy oxides.

4. CONCLUSION

The study of semiconducting Ag–Cu mixed oxides grown by anodic oxidation indicated that, whenever the oxidized metallic alloy was single phase, a single-phase oxide was obtained, while metallic alloys of two or three Ag–Cu phases yielded more than one oxide phase. A few days after growth, either the multiphase oxide samples dissociated to Cu_2O and silver or the Cu_2O present induced the dissociation of the mixed oxide. The single-phase oxides had a relatively long lifetime. It may be interesting to try the anodization and photovoltaic study described here on metastable Ag–Cu alloys resulting from ultrafast quenching techniques.

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