JOURNAL OF MATERIALS SCIENCE 21 (1986) 985–988

# Preparation and photovoltaic properties of anodically grown $Ag_2O$ films

E. TSELEPIS, E. FORTIN
*Department of Physics, University of Ottawa, Ottawa, Canada*

The semiconducting and photovoltaic properties of p-type $Ag_2O$ films grown anodically on silver electrodes were studied, in view of possible applications in solar energy conversion. Films were grown in different alkaline solutions; the best results were obtained for 0.02M $Ag_2SO_4$ + 0.17M $NH_4OH$ + $5.7 \times 10^{-3}$M $Ba(OH)_2$ saturated with $Ag_2O$ powder, stirred mechanically at room temperature. Film thicknesses of up to 10 $\mu$m were thus obtained for the first time in anodically grown $Ag_2O$. Photovoltaic spectra taken at 300 K give a bandgap of $E_g = 1.42 \pm 0.04$ eV. Evaporated gold on $Ag_2O$ appears to be ohmic while aluminium and platinum are rectifying. The barrier height of $Ag/Ag_2O$ is $0.90 \pm 0.02$ eV, that of $Al/Ag_2O$ is $0.93 \pm 0.02$ eV, and that of platinum $0.94 \pm 0.02$ eV. The best cells give an open-circuit voltage, $V_{oc}$, of over 150 mV, and a short circuit current, $I_{sc} = 100\,\mu A\,cm^{-2}$ under $50\,mW\,cm^{-2}$ illumination.

## 1. Introduction

In view of possible applications in solar energy conversion, the photovoltaic properties of anodically grown $Ag_2O$ were investigated. The work was motivated by the fact that $Ag_2O$ has a direct energy gap of about 1.4 eV [1–3] making it perfectly suited for absorption of the solar spectrum [4]. $Ag_2O$ is the only structural analogue of $Cu_2O$, which has been prepared thermally as well as anodically [5, 6] and it would be interesting to compare their properties. In the polycrystalline form $Ag_2O$ has a dark grey to brown colour [7], and like $Cu_2O$ has a relatively high specific resistivity.

Anodic oxidation was preferred over other methods of preparation of $Ag_2O$ for the following reasons:

1. the working conditions are easily controlled;
2. there is the prospect of making polycrystalline samples of any desired dimensions, an important consideration for solar panel construction.

Even though there has been quite a large amount of research work done on anodic oxidation of silver to $Ag_2O$ by electrochemists [8–14], interest has been restricted to very thin (a few tens of nanometres) oxide films used to investigate reaction potentials or growth processes. In one case [15, 16] there were attempts at electrical and photoelectrical measurements. The goal here was to grow compact micrometre-thick oxide films of large crystals on relatively large silver sheets.

In the following sections we first discuss the techniques used for anodically growing thick $Ag_2O$ films of relatively good quality. The photovoltaic properties are then considered, allowing the determination of the material's band gap and conductivity type. Finally, the barrier height of some metals with $Ag_2O$ is measured.

## 2. Sample preparation

A standard electrolytic cell was used for anodic oxidation. The silver used was in the form of 0.5 mm thick sheets of 99.99% purity. The sheets were cut in rectangular electrodes of dimensions 3.75 cm × 1.25 cm. Before being introduced to the solution, the silver plates were degreased with ethanol, polished with silverware polish, rinsed with distilled water and dried with ethanol. This procedure leaves the silver surface reasonably clean with minute scratches. The two silver electrodes were then mounted parallel to each other, spaced 0.5 cm apart on a holder.

All solutions for oxidation were prepared from reagent grade chemicals and distilled water. A Hg/HgO reference electrode was used occasionally for calibration purposes. Stirring kept the temperature of the oxidizing solutions constant; it also prevented the accumulation of oxidized constituents and supplied sufficient reactants for a critical reaction on the electrode, so that the equilibrium potential did not increase, leading to an early passivation before the desired thickness and uniform coverage were obtained.

In the constant current silver anodic oxidation process, there are two very well defined plateaus [17]. The first plateau represents the oxidation of silver to $Ag_2O$ and the second that of $Ag_2O$ to AgO. Between the two plateaus there is a very sharp increase of potential, indicating the transition from $Ag_2O$ to AgO growth. During preliminary galvanostatic runs, it was noticed that these features were kept intact in the anode–cathode potential against time diagrams. The use of the reference electrode was therefore not necessary except for calibration purposes. Having as a guide the potential against pH equilibrium diagram of silver [18] different solutions were tried. First, an $Ag_2SO_4$ solution was tried, which only oxidized a very thin layer of silver. More highly alkaline solutions were then tried, such as NaOH and KOH, of different pH and at various temperatures ranging from 20 to

0022–2461/86 $03.00 + .12

90° C. These solutions resulted in the first significant growth of $Ag_2O$; the coverage, however, was often incomplete and the films gave little photovoltaic effect. Finally, the solution that gave the best results was 0.02M $Ag_2SO_4$ + 0.17M $NH_4OH$ + $6 \times 10^{-3}$M $Ba(OH)_2$, saturated with $Ag_2O$ powder at room temperature (pH = 11.6). Typical oxidizing conditions were: light stirring, constant current density of about 2 mA $cm^{-2}$ and duration of oxidation of 1 to 3 h.

There is general agreement in the literature (8, 15–17) that oxidation starts as a dissolution–precipitation process. There are indications, however, that as the oxide grows, a parallel mechanism of a compact film formation exists as a result of a direct interfacial reaction [15, 17, 19, 20]; therefore, there is evidence for a dual layer oxide with adsorbed oxygen at the oxide–solution interface. In our solution, $Ag_2SO_4$ acts as supplier of $Ag^+$ ions to the solutions, $NH_4OH$ is responsible for the initial dissolution–precipitation mechanism, while keeping the pH within the desired range. $Ba(OH)_2$ is added to absorb any carbon, carbon monoxide or carbon dioxide in the solution, to form an insoluble precipitate $BaCO_3$, thus preventing $Ag_2O$ from absorbing any carbon during its formation. The dissolution–precipitation process consists of $Ag^+$ dissolution and oxide deposition on the anode, initially in the form of islands which were grown from phase nucleation centres. This is the so-called primary layer [19]. The thickness of this layer is of the order of a few tens of nanometres and the coverage is not complete. Further dissolution of $Ag^+$ from the silver electrode becomes increasingly difficult as the primary layer expands and thickens. Then the secondary layer [19] starts building up with $Ag^+$ diffusion through the oxide. This layer consists of primary centres that are reported in the literature to grow laterally up to 1 $\mu$m [21]. In the present case they grow between 5 and 20 $\mu$m, overlapping each other and covering the silver surface totally. Therefore, some new process has taken over, leading to larger crystals. This process is possibly either the direct interfacial reaction mentioned above or a precipitation process due to the composition of the solution. The prospect of having a dual oxide layer has to be investigated because it would affect the semiconducting and photovoltaic properties of the oxide.

In a recent attempt to improve the silver surface condition prior to oxidation, the electrodes were annealed at 860° C in air for several hours before anodic oxidation. In this way single silver crystals, some of area 1 to 2 $mm^2$, were formed. It was noticed that the oxide crystallites on some silver crystals grew in the form of a flat mosaic instead of the pyramidal texture of previous samples. The texture of the oxide film appears to depend on the orientation of the silver crystals on the electrode, as was mentioned by Fleischmann *et al.* [17]. Such films give stronger photovoltaic (PV) signals and exhibit better electrical stability.

X-ray powder photographs of $Ag_2O$ scratched off the samples showed no other silver oxide phase to be present, to the degree of accuracy this technique provides. Scanning electron microprobe and Auger analysis were attempted but due to the small bond dissociation energy (Ag–O $\simeq$ 1.5 eV), $Ag_2O$ is partially reduced under the electron probing beams: the technique only identified sulphur, chlorine and carbon as trace impurities present in the oxide. The thickness of the oxide film has been estimated by the Coulombmetric method (assuming 100% efficiency of the process an upper thickness limit is obtained) and by direct microscopic observation of $Ag_2O$ film cross-sections. Thicknesses ranged from 2 to 10 $\mu$m, varying locally due to the relief of the pyramidal polycrystalline texture.

## 3. Photovoltaic properties

The PV properties of metal/anodic $Ag_2O$ Schottky junctions were examined from spectra taken at room temperature. Such measurements can yield the energy gap and determine the Schottky barrier height for different metals. The metallic contacts were deposited in a Veeco cryopumped evaporator. The thickness of the metallic films ranged from 7 to 10 nm, allowing the light to reach the oxide–metal interface without appreciable absorption.

A large number of PV spectra on more than 100 samples were taken with different rectifying metal contacts. In Figs. 1 and 2 typical PV spectra are presented. Fig. 1 shows the spectrum of an $Ag/Ag_2O/Ag$ sandwich with an $Ag_2O$ thickness of about 1 $\mu$m. In this case we have two opposing junctions. For $\lambda <$ 540 nm the front junction is active and for $\lambda >$ 540 nm the back junction takes over, as indicated by the sign reversal of the photosignal. Fig. 2 shows the PV spectrum of an $Ag/Ag_2O/Au$ (ohmic) cell with a good spectral response and an energy gap of about 1.44 eV. Even though $Ag_2O$ is a direct bandgap semiconductor, no steep decrease in the photoresponse was observed below the energy gap: in the PV spectra of Figs. 1 and 2 there is a spectral spread of 100 to 150 nm between the peak photoresponse and half the maximum photoresponse, where the bandgap is expected to be according to the Moss criterion [22]. This relatively long tail could be due to impurities (sulphur, chlorine, carbon) and structural defects in the oxide, resulting in level distribution extending well into the gap; at the same time, variable oxygen concentration across the oxide film would cause grading of the

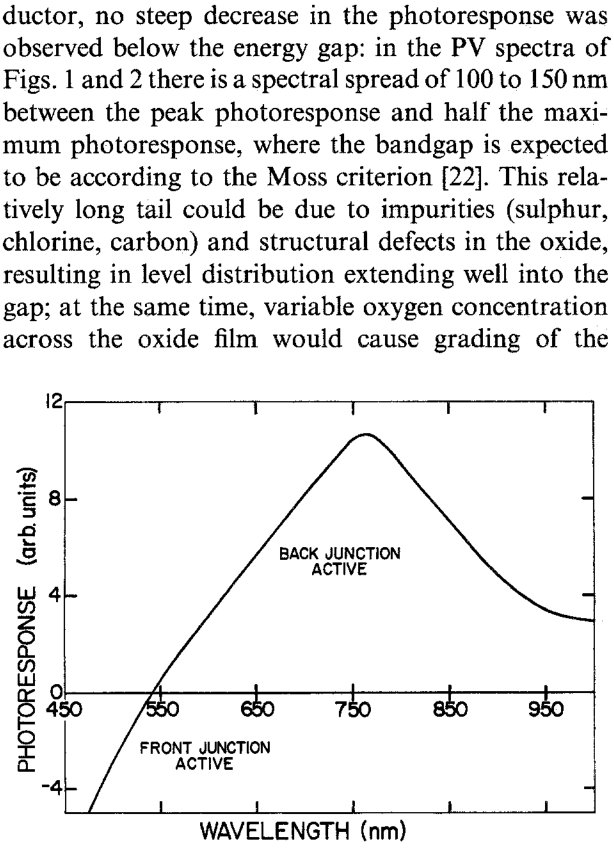

*Figure 1* Photovoltaic spectrum of an $Ag/Ag_2O/Ag$ cell.

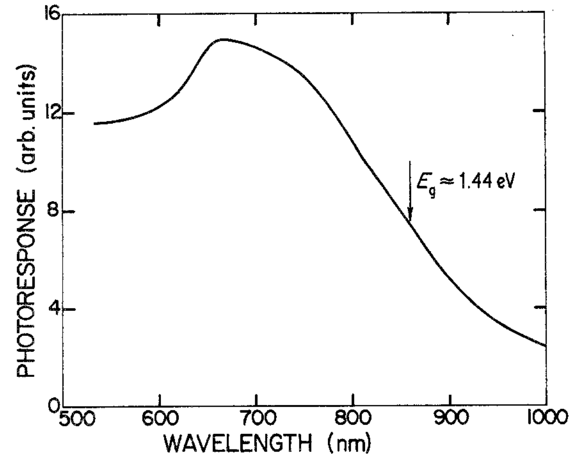

*Figure 2* Photovoltaic spectrum of an Au/$Ag_2O$/Ag cell.

bandgap. The value of the $Ag_2O$ bandgap at room temperature, considering the Moss criterion [22], averaged over a large number of samples is 1.42 ± 0.04 eV. As grown, $Ag_2O$ was p-type as determined by a comparison of the sign of its PV signal to that of an equivalent Cu/p-type $Cu_2O$ cell.

## 4. Schottky barrier measurements

For thin ($\sim 1\,\mu$m) films the back junction of $Ag_2O$/Ag was usually active for illumination with bandgap light. With thicker films ($\sim 10\,\mu$m) the front junction was active even at energies below the gap, making it possible to determine the barrier height of $Ag_2O$ with other metals. The barrier heights were obtained for aluminium and platinum, using the photoelectric method. This method was preferred because the values were directly derived from the PV spectra and more importantly did not necessitate the application of any voltage to the electrically fragile cells. The observed barrier heights are: 0.90 ± 0.02 eV for Ag/$Ag_2O$ (Fig. 3), 0.93 ± 0.02 eV for $Ag_2O$/Al (Fig. 4) and 0.94 ± 0.02 eV for $Ag_2O$/Pt; gold is ohmic, when evaporated in conditions which do not cause oxide reduction (i.e. pressure less than $6 \times 10^{-6}$ torr and evaporation over a 1 to 2 min period for a 7 to 10 nm film).

All barrier heights obtained are the same within experimental error. This indicates that either the barrier is surface state controlled, or as for $Cu_2O$ [23] the front barrier is dictated by the partial reduction of the $Ag_2O$ surface induced by the evaporated metals (see the case of gold above) and subsequent interdiffusion phenomena. Another possibility is that the silver print contact used between the evaporated metal layer and the electrical leads could perhaps diffuse through the 7 to 10 nm evaporated metal causing the same effect. Attempts will be made to determine the barrier height of other metals with $Ag_2O$, possibly avoiding the use of silver print for the electrical contacts.

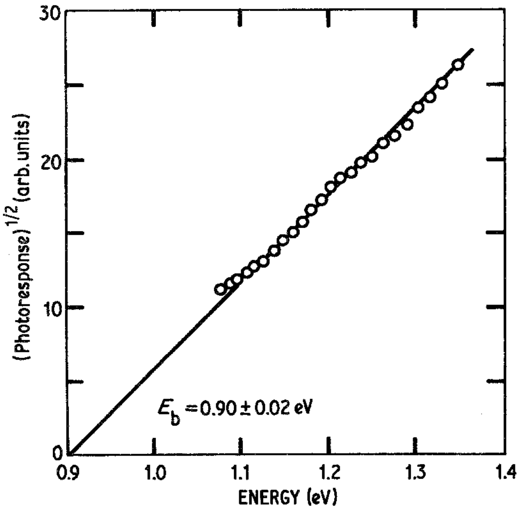

*Figure 3* Barrier height of an $Ag_2O$/Ag junction.

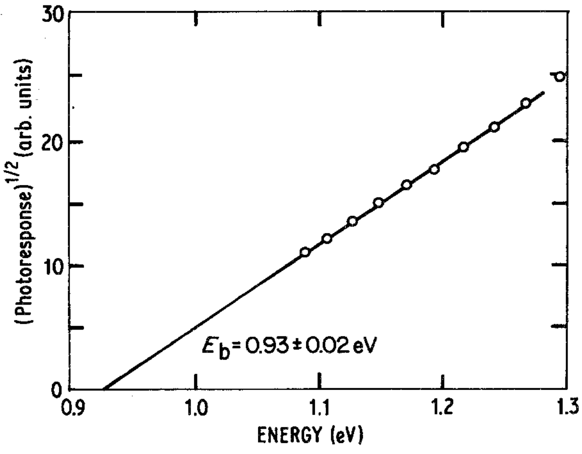

*Figure 4* Barrier height of $Ag_2O$/Al.

So far the Schottky barrier cells are not very efficient solar cells, in part because of the polycrystalline structure of the $Ag_2O$ film, which creates a large number of grain boundaries and thus reduces the recombination time. The best cells give a $V_{oc}$ of over 150 mV and $J_{sc} \simeq 100\,\mu$A cm$^{-2}$ under 50 mW cm$^{-2}$ illumination with a quartz iodine lamp.

## 5. Conclusion

The PV spectra discussed here were taken with fast chopped light techniques, masking a number of slow PV effects such as the evolution of the photosignal with time (over seconds) and sometimes even sign reversal. Such effects have been observed in anodically grown $Cu_2O$ as well [5] and remain largely unexplained. Difficulties also arise from electrical breakdown and poor thermal stability of the oxide films. With improvement of the film quality more fundamental studies can be attempted on $Ag_2O$, such as gap variation with temperature, effective mass determination and exciton studies.

## References

1. T. L. ROLLINS and F. L. WEICHMAN, *Phys. Status. Solidi* **15** (1966) 233.
2. F. I. KREINGOLD and B. S. KULINKIN, *Sov. Phys. Semicond.* **4** (1971) 2022.
3. E. FORTIN and F. L. WEICHMAN, *Phys. Status Solidi* **5** (1964) 515.
4. E. F. GROSS and F. I. KREINGOLD, *Opt. i Spectroskopia* **10** (1961) 417.
5. E. FORTIN and D. MASSON, *Solid State Electron.* **25** (1982) 281.
6. E. FORTIN and W. M. SEARS, *Can. J. Phys.* **60** (1982) 901.
7. J. C. BAILLARD, in "Comprehensive Inorganic Chemistry" (Pergamon Press, New York, 1973) pp. 97–8.

8. B. V. TILAK, R. S. PERKINS, H. A. KOZLOWSKA and B. E. CONWAY, *Electrochim. Acta* **17** (1972) 1447.
9. T. P. DIRSKE, *J. Electrochem. Soc.* **106** (1959) 453.
10. C. P. WALES and J. BURBANK, *ibid.* **106** (1959) 885.
11. T. P. DIRSKE, *ibid.* **106** (1959) 920.
12. T. P. DIRSKE, D. DEWIT and R. SHOEMAKER, *ibid.* **114** (1967) 1196.
13. W. J. HAMER and D. N. GRAIG, *ibid.* **104** (1957) 206.
14. B. D. CAHAN, J. B. OCKERMAN, R. F. AMLIC and P. RUETSCHI, *ibid.* **107** (1960) 725.
15. M. J. DIGNAM, H. M. BARRETT and G. D. NAGY, *Can. J. Chem.* **47** (1969) 4253.
16. D. B. GIBBS, B. RAO, R. A. GRIFFIN and M. J. DIGNAM, *J. Electrochem. Soc.* **122** (1975) 1167.
17. M. FLEISCHMANN, D. J. LAX and H. R. THIRSK, *Trans. Faraday Soc.* **64** (1968) 3128.
18. MARCEL POURBAIX, in "Atlas of Electrochemical Equilibria in Aqueous Solutions" (Pergamon Press, Oxford, and Cebelcor, Brussels, 1966) p. 396.
19. G. W. D. BRIGGS, M. FLEISCHMANN and D. J. LAX, *Trans. Faraday Soc.* **64** (1968) 3120.
20. V. I. VESELOVSKY, T. I. BORISOVA, A. A. JAKOVLEVA and S. O. IZIDINOV, *Electrochim. Acta* **10** (1965) 325.
21. S. YOSHIZAWA and Z. TAKEHARA, *J. Electrochem. Soc. Jpn.* **31** (1963) 91.
22. T. S. MOSS, in "Photoconductivity in the Elements" (Butterworth, London, 1952) pp. 31–4.
23. L. C. OLSEN, R. C. BOHARA and M. W. URIE, *Appl. Phys. Lett.* **34** (1979) 47.

*Received 28 January*
*and accepted 30 May 1985*